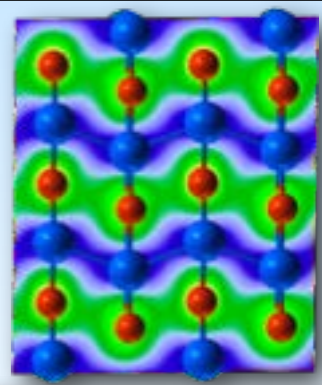




# Computational Discovery and Design of Materials for Energy Technologies and Electronic Devices

Richard G. Hennig, Cornell University

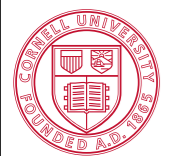
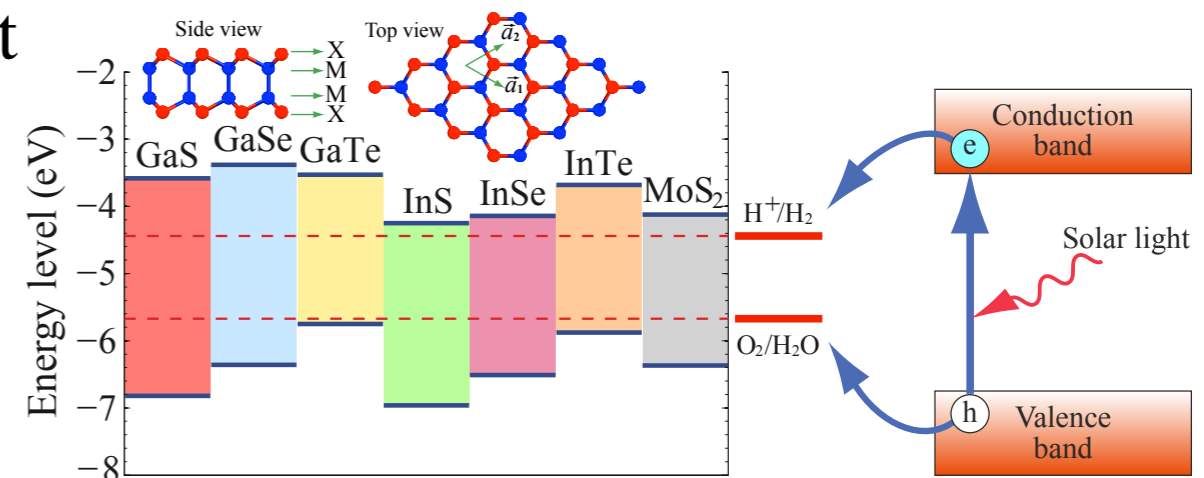


## Data mining for novel 2D materials

boron 5 <b>B</b> 10.811	nitrogen 7 <b>N</b> 14.007			carbon 6 <b>C</b> 12.011					
aluminium 13 <b>Al</b> 26.982	phosphorus 15 <b>P</b> 30.974	beryllium 4 <b>Be</b> 9.0122	zinc 30 <b>Zn</b> 65.38	oxygen 8 <b>O</b> 15.999	silicon 14 <b>Si</b> 28.086	titanium 22 <b>Ti</b> 47.867	vanadium 23 <b>V</b> 50.942		sulfur 16 <b>S</b> 32.065
gallium 31 <b>Ga</b> 69.723	arsenic 33 <b>As</b> 74.922	magnesium 12 <b>Mg</b> 24.305	cadmium 48 <b>Cd</b> 112.41			zirconium 40 <b>Zr</b> 91.224	niobium 41 <b>Nb</b> 92.906	molybdenum 42 <b>Mo</b> 95.96	selenium 34 <b>Se</b> 78.96
indium 49 <b>In</b> 114.82	antimony 51 <b>Sb</b> 121.76	calcium 20 <b>Ca</b> 40.078	mercury 80 <b>Hg</b> 200.59			hafnium 72 <b>Hf</b> 178.49	tantalum 73 <b>Ta</b> 180.95	tungsten 74 <b>W</b> 183.84	platinum 78 <b>Pt</b> 195.08

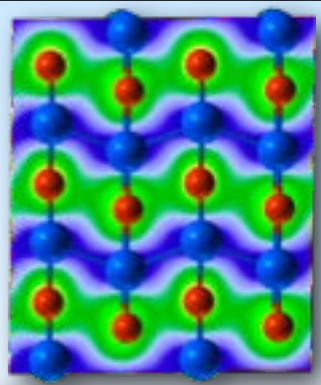
Novel 2D materials with low formation energies show unique structures that can be stabilized on metal substrates, have useful electronic properties that can be tuned by strain, and can be stable in aqueous environment

APL 101, 153109 (2012), PRB 87, 184114 (2013),  
PRB 87, 165415 (2013), Chem. Mater. 25, 3232 (2013),  
J. Phys. Chem. C, in print (2013)



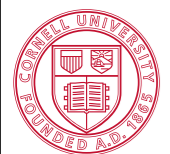
# Computational Discovery and Design of Materials for Energy Technologies and Electronic Devices

Richard G. Hennig, Cornell University



## Acknowledgement

- Genetic algorithm development: W. Tipton, B. Revard, S. Wenner, A. Sanchez
- Battery materials: W. Tipton, C. Bealing, K. Matthew, M. Blonsky
- Single-layer materials: H. Zhuang, A. Singh, M. Spencer, J. Park
- Financial support by EMC<sup>2</sup>, CCMR, NSF-CAREER
- Computational resources provided by XSEDE, Teragrid, CCNI



## GASP Genetic Algorithm for Structure Prediction

<http://gasp.mse.cornell.edu>  
J. Phys. Cond. Matter, submitted (2013)  
Invited book chapter, Springer (2013)

## VASPsol and QMCsol Solvation Module for DFT and QMC

Phys. Rev. B 85, 201102(R) (2012)  
Phys. Rev. B, in preparation (2013)

Method and Algorithm Development

## Computational Discovery and Design of Materials

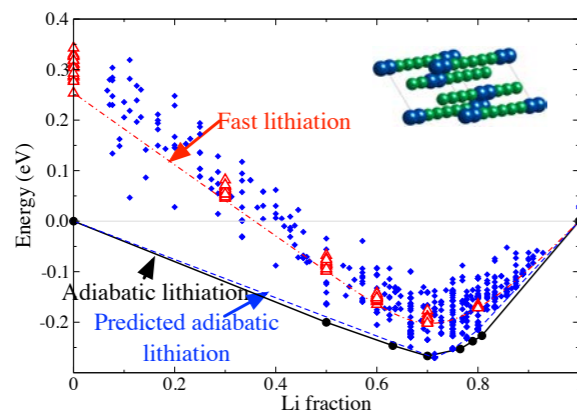
Application to Materials for Energy Applications

3D

2.5D

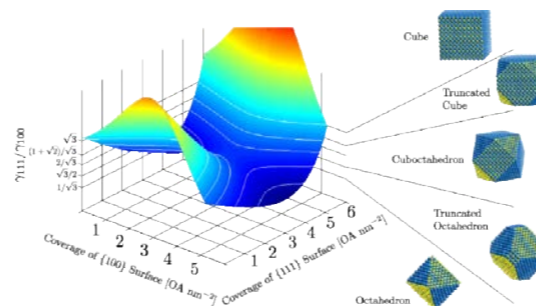
2D

### Battery electrodes and materials under pressure



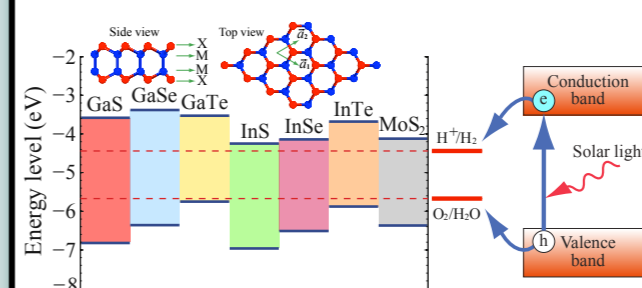
Nature 451, 445 (2008)  
Phys. Rev. B 82, 014101 (2010)  
Phys. Rev. B 83, 224102 (2011)  
Phys. Rev. B 87, 184114 (2013)

### Nanocrystals surfaces and chemical transformations

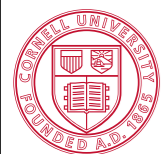


ACS Nano 6, 2118 (2012)  
Phys. Rev. B 87, 245402 (2013)  
J. Phys. Chem. C 117, 14303 (2013)  
Nanoletters 12, 4530 (2012)

### Novel 2D materials for electronic and energy applications



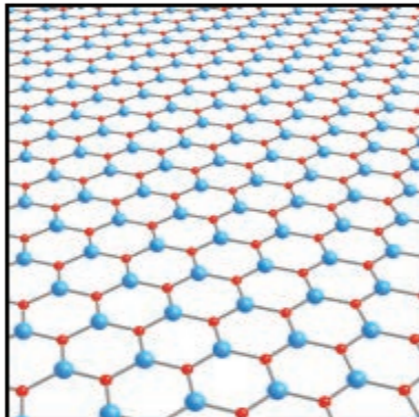
Appl. Phys. Lett. 101, 153109 (2012)  
Phys. Rev. B 87, 165415 (2013)  
Phys. Rev. B 87, 094112 (2013)  
Chem. Mat., 25, 3232 (2013)  
Appl. Phys. Lett. submitted (2012)  
J. Phys. Chem. C, submitted (2013)

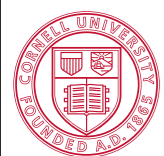


# Materials Discovery by Data-Mining Single-Layer Materials

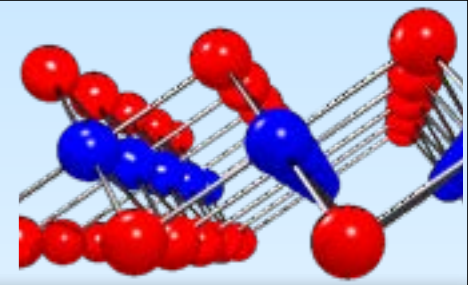
## For Electronic Devices and Energy Technologies

Houlong Zhuang, Arunima Singh, Richard G. Hennig

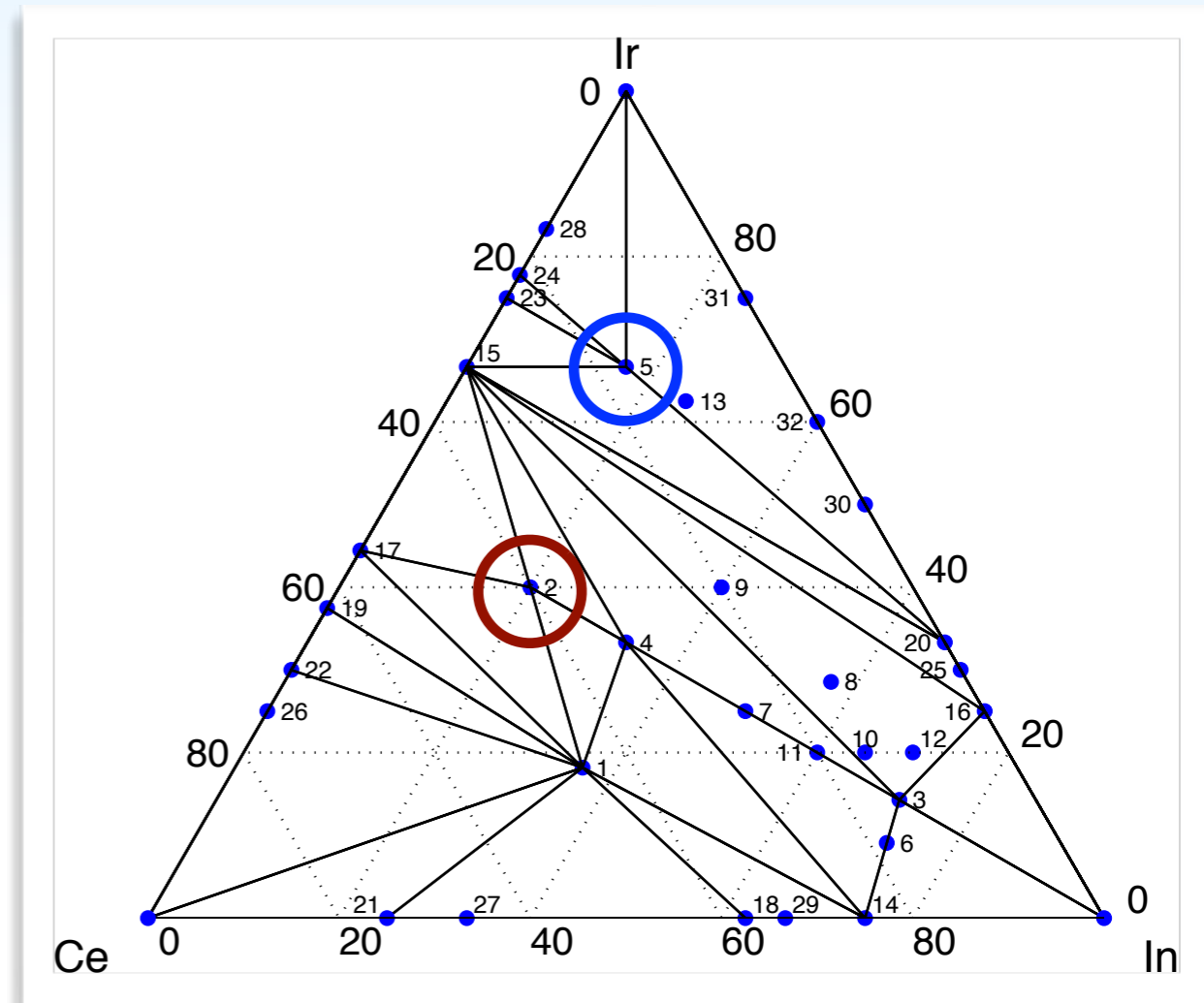
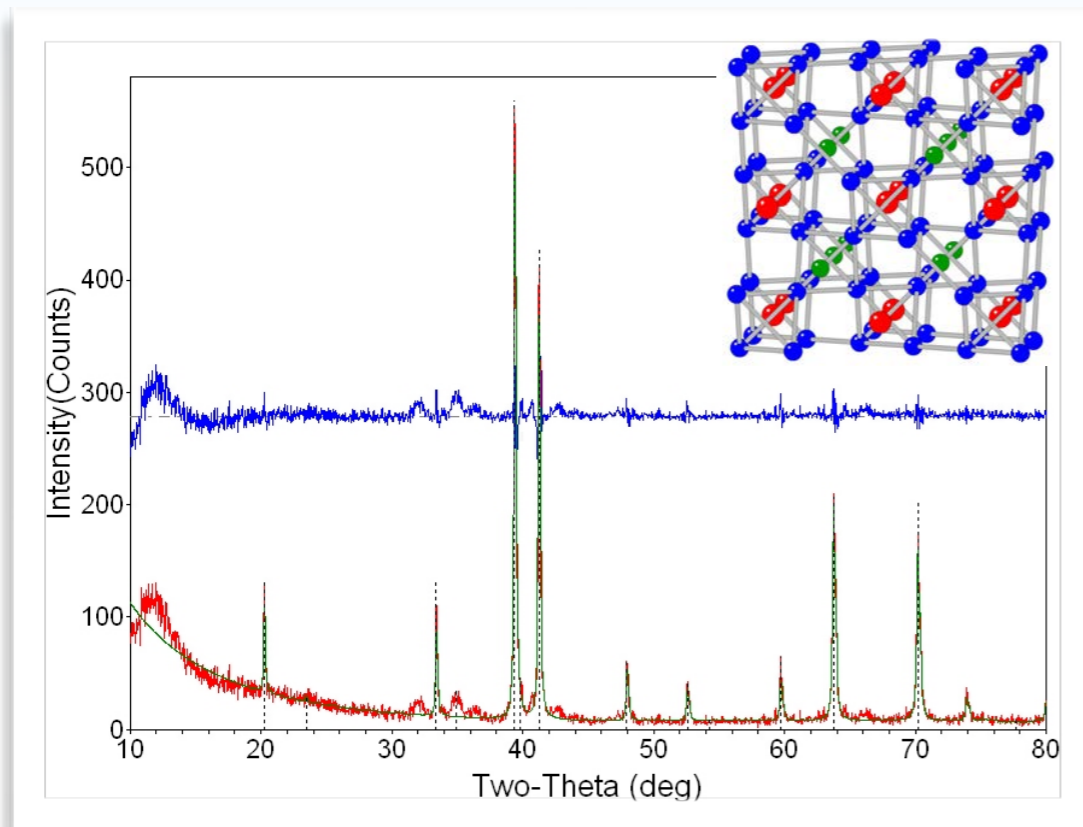
boron 5 <b>B</b> 10.811	nitrogen 7 <b>N</b> 14.007			carbon 6 <b>C</b> 12.011					
aluminium 13 <b>Al</b> 26.982	phosphorus 15 <b>P</b> 30.974	beryllium 4 <b>Be</b> 9.0122	zinc 30 <b>Zn</b> 65.38	oxygen 8 <b>O</b> 15.999	silicon 14 <b>Si</b> 28.086	titanium 22 <b>Ti</b> 47.867	vanadium 23 <b>V</b> 50.942		sulfur 16 <b>S</b> 32.065
gallium 31 <b>Ga</b> 69.723	arsenic 33 <b>As</b> 74.922	magnesium 12 <b>Mg</b> 24.305	cadmium 48 <b>Cd</b> 112.41			zirconium 40 <b>Zr</b> 91.224	niobium 41 <b>Nb</b> 92.906	molybdenum 42 <b>Mo</b> 95.96	selenium 34 <b>Se</b> 78.96
indium 49 <b>In</b> 114.82	antimony 51 <b>Sb</b> 121.76	calcium 20 <b>Ca</b> 40.078	mercury 80 <b>Hg</b> 200.59			hafnium 72 <b>Hf</b> 178.49	tantalum 73 <b>Ta</b> 180.95	tungsten 74 <b>W</b> 183.84	platinum 78 <b>Pt</b> 195.08



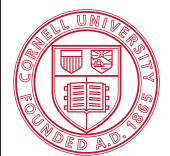
# Discovery of Ternary Intermetallics by Datamining



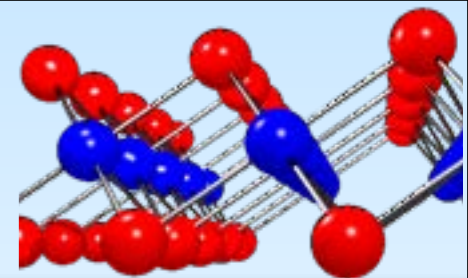
- Use similarities between materials systems, e.g, similar binary phases to identify candidate structures in databases such as ICSD
- Calculate phase stability
- Synthesize novel materials



**Discovery of two new compounds:  $\text{CeIr}_4\text{In}$  and  $\text{Ce}_2\text{Ir}_2\text{In}$**   
**Successful synthesis of  $\text{CeIr}_4\text{In}$**



# Why Single-Layer Materials?

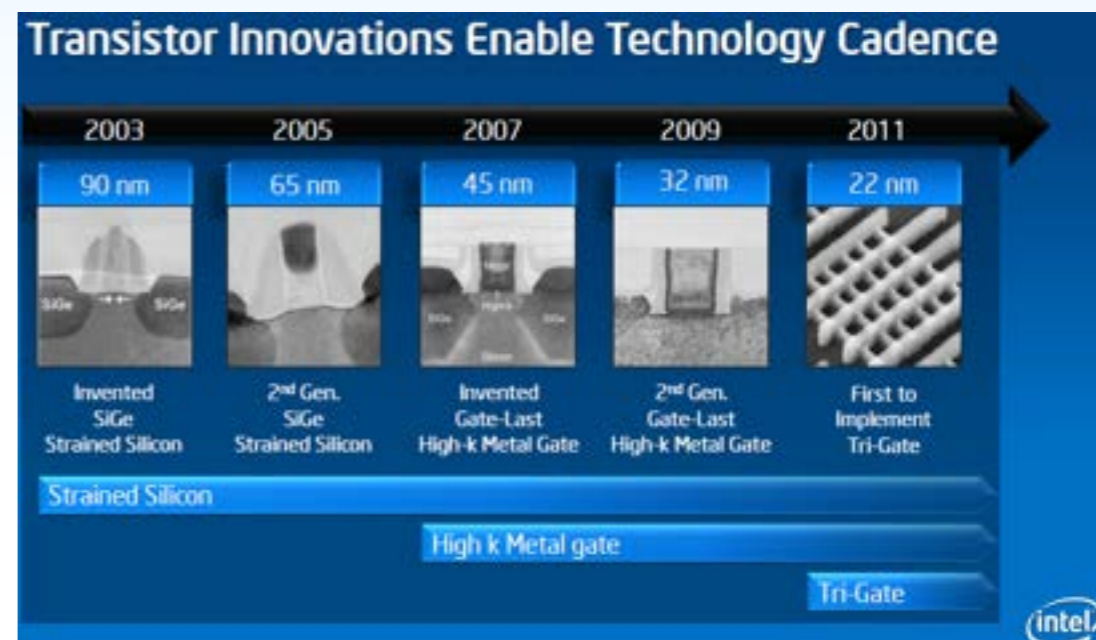


## Materials interfaces

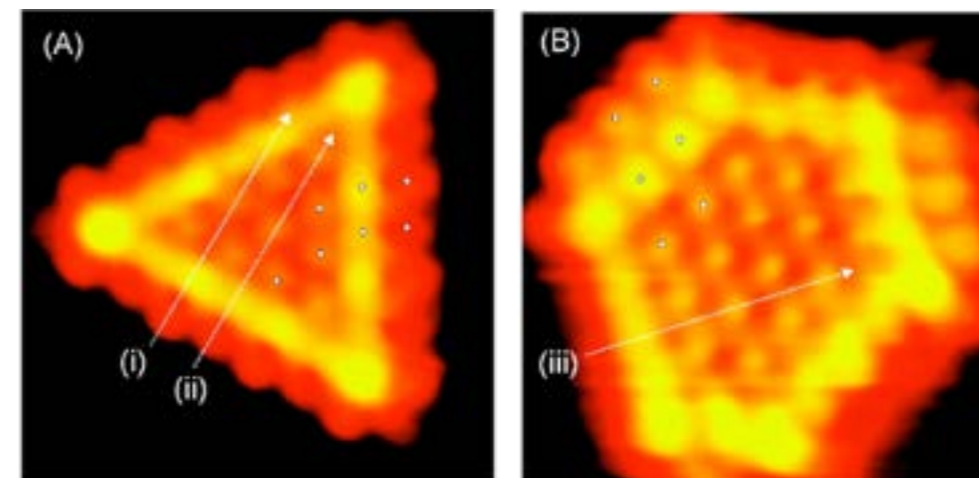
- At the heart of essentially all modern-day critical technologies
- Importance of interfaces in key industrial segments:  
Microelectronics, chemical and energy industries

## Single-layer or 2D materials

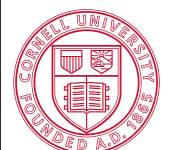
- Maximize their interfacial area
- New class of materials
- Properties differ from 3D counterparts
- Example of synthesized 2D materials:  
Graphene, BN, ZnO, MoS<sub>2</sub>, WSe<sub>2</sub>, and SnS<sub>2</sub>
- Potentially many more 2D materials awaiting discovery



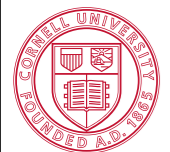
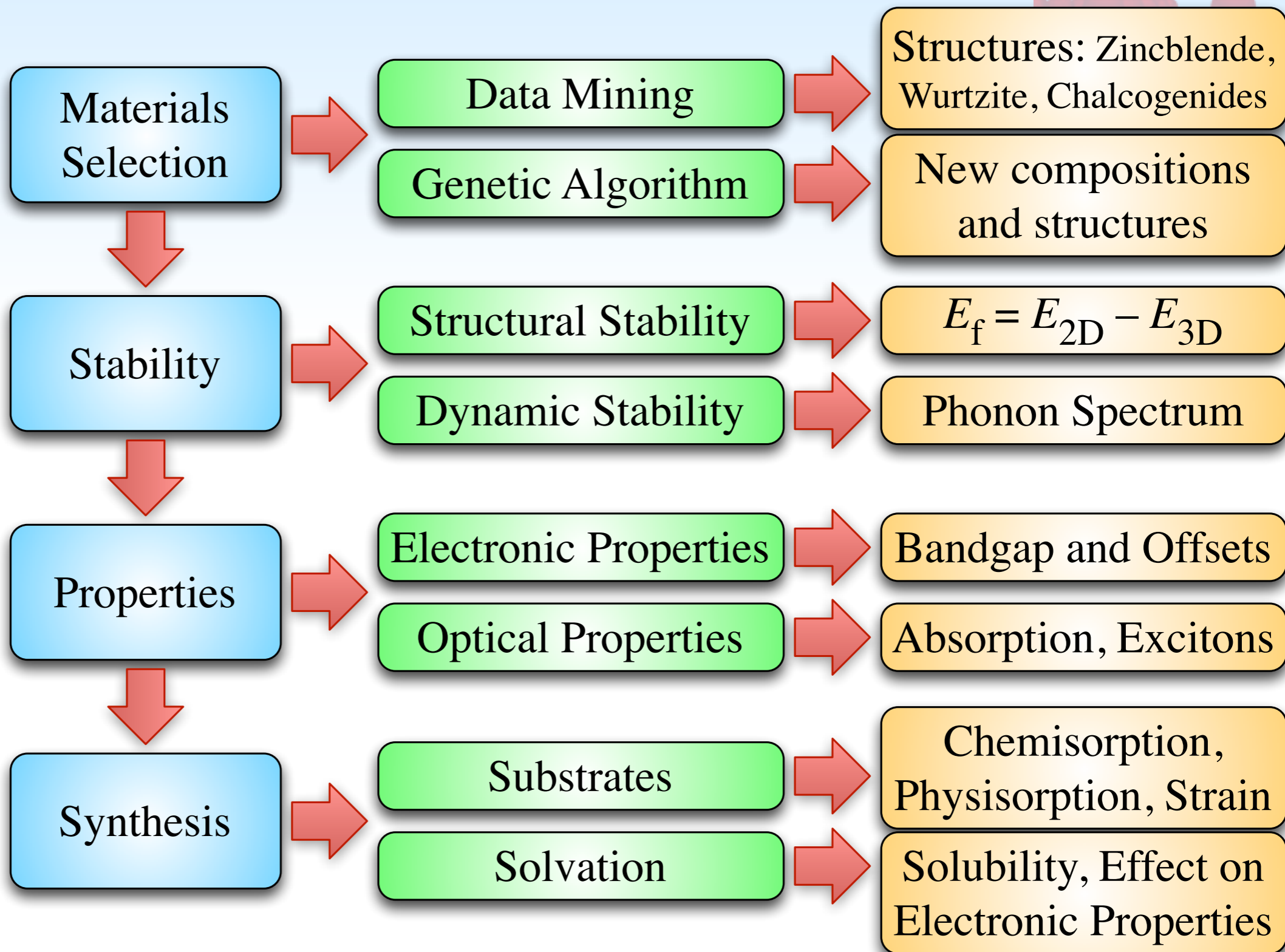
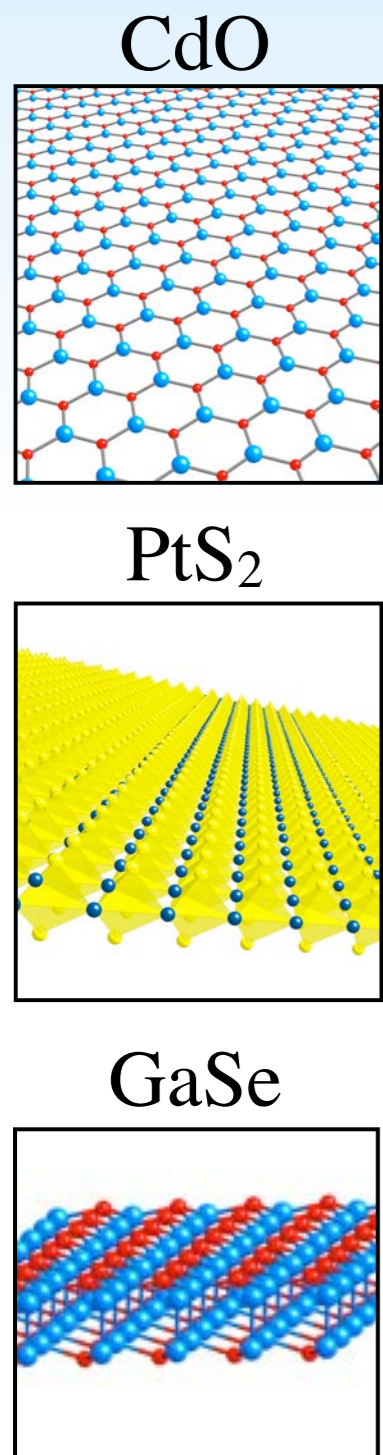
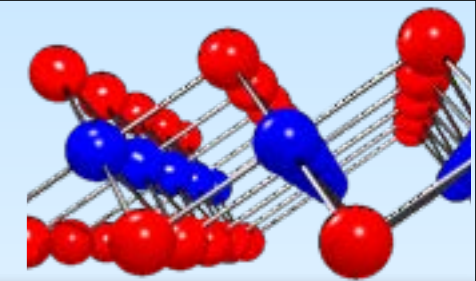
<http://newsroom.intel.com/docs/DOC-2032>



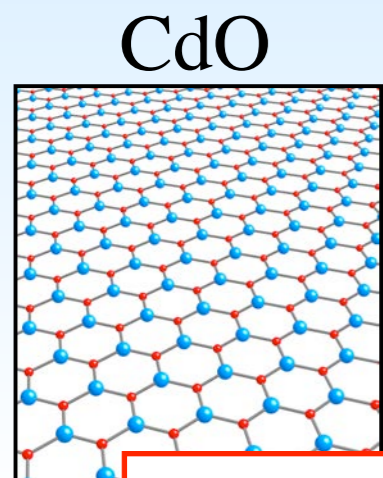
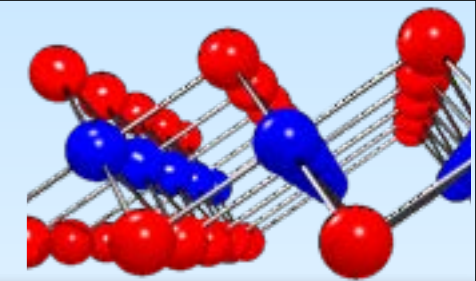
Lauritsen et al., J. Catalysis 221 25 (2004)



# Discovery of Single-Layer Materials



# Discovery of Single-Layer Materials



Materials Selection

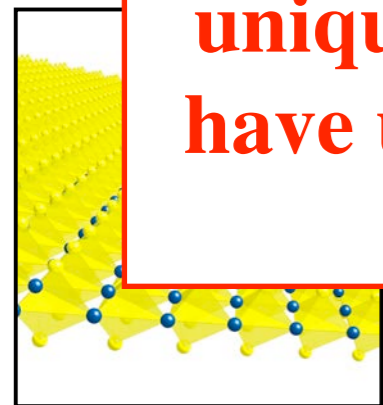
Data Mining

Genetic Algorithm

Structures: Zincblende, Wurtzite, Chalcogenides

New compositions and structures

**Novel 2D materials with low formation energies show unique structures that can be stabilized on metal substrates, have useful electronic properties that can be tuned by strain, and can be stable in aqueous environment**



Properties

Electronic Properties

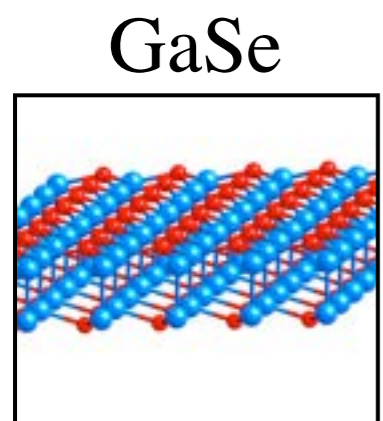
Optical Properties

3D

um

Offsets

Absorption, Excitons



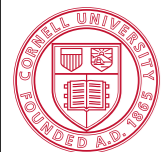
Synthesis

Substrates

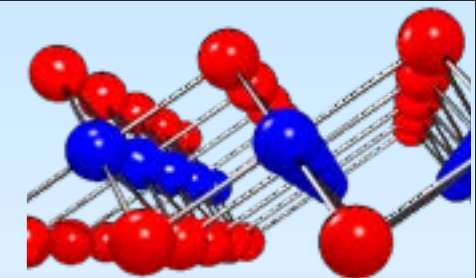
Solvation

Chemisorption, Physisorption, Strain

Solubility, Effect on Electronic Properties



# Data Mining for 2D Materials



- Search International Crystal Structure Database (ICSD) for candidates
- Same 3D bulk structure as C, BN, ZnO, SiC, MoS<sub>2</sub>

**Summary** Collection Code 77087

Struct.formula	Ga P	Author	Rabadanov, M.Kh.; Loshmanov, A.A.; Shaldin, Yu.V.
Space Group	F -4 3 m(216)	Title of Article	Anharmonic thermal vibrations of atoms in crystals with sphalerite structure - Ga P, Zn S, Zn Se, and Zn Te: High-temperature X-ray studies
Unit Cell	5.448(1) 5.448 5.448 90. 90. 90.	Reference	Kristallografiya (1997) 42, p649-p659
Cell Volume	161.70 Å <sup>3</sup>	Formula Units per Cell	4
Temperature	293 K	Pressure	atmospheric
PDF-numbers	01-071-5973 32-397	R-value	0.0072
Remark	High Quality Data		

[Export CIF File](#)  [Show Synoptic View](#) [Feedback to the ICSD Editor](#)

**Details**

Expand All Collapse All

- Visualization
- Chemistry
- Published Crystal Structure Data
- Standardized Crystal Structure Data

Cell Parameters	5.4480 5.4480 5.4480 90.000 90.000 90.000				
Volume	161.70	Formula Units per Cell	4	Calc. Dens.	4.14
Space Group	F -4 3 m(216)	Pearson Symbol	cF8		
Crystal System	cubic	Crystal Class	-43m	Laue Class	m-3m
Wyckoff Sequence	c a				
Axis Ratios	a/b 1.0000	b/c 1.0000	c/a 1.0000		
Transformation Method	Tidy				
Transformation Info	Multiple transformations possible, first one selected				

Remark

EL	Lbl	OxState	WyckSymb	X	Y	Z	U	SOF
Ga	1	+3.00	4a	0.0000	0.0000	0.0000	0.0073	
P	1	-3.00	4c	0.2500	0.2500	0.2500	0.0070	

[Distances & Angles](#)  
[Bibliography](#)  
[Experimental Information](#)  
[Warnings & Comments](#)  
[Compare Published & Standardized Structure](#)

## Wurtzite and zincblende

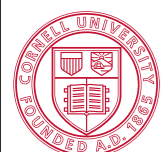
- 96 unique binaries
- III-V, II-VI, I-VII families, and others

## 2H and 1T MoS<sub>2</sub> structure

- 26 unique binary entries
- Many transition metal dichalcogenides

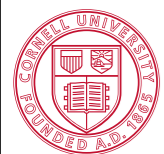
## Other layered 3D bulk materials

- Group-III monochalcogenides

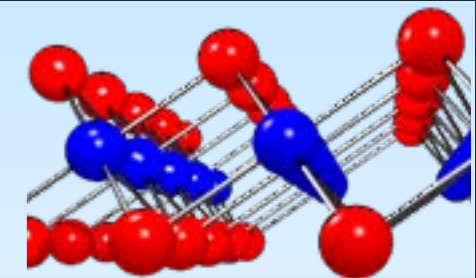


# **Discovery and Virtual Synthesis of 2D III-V Materials for Electronic Applications**

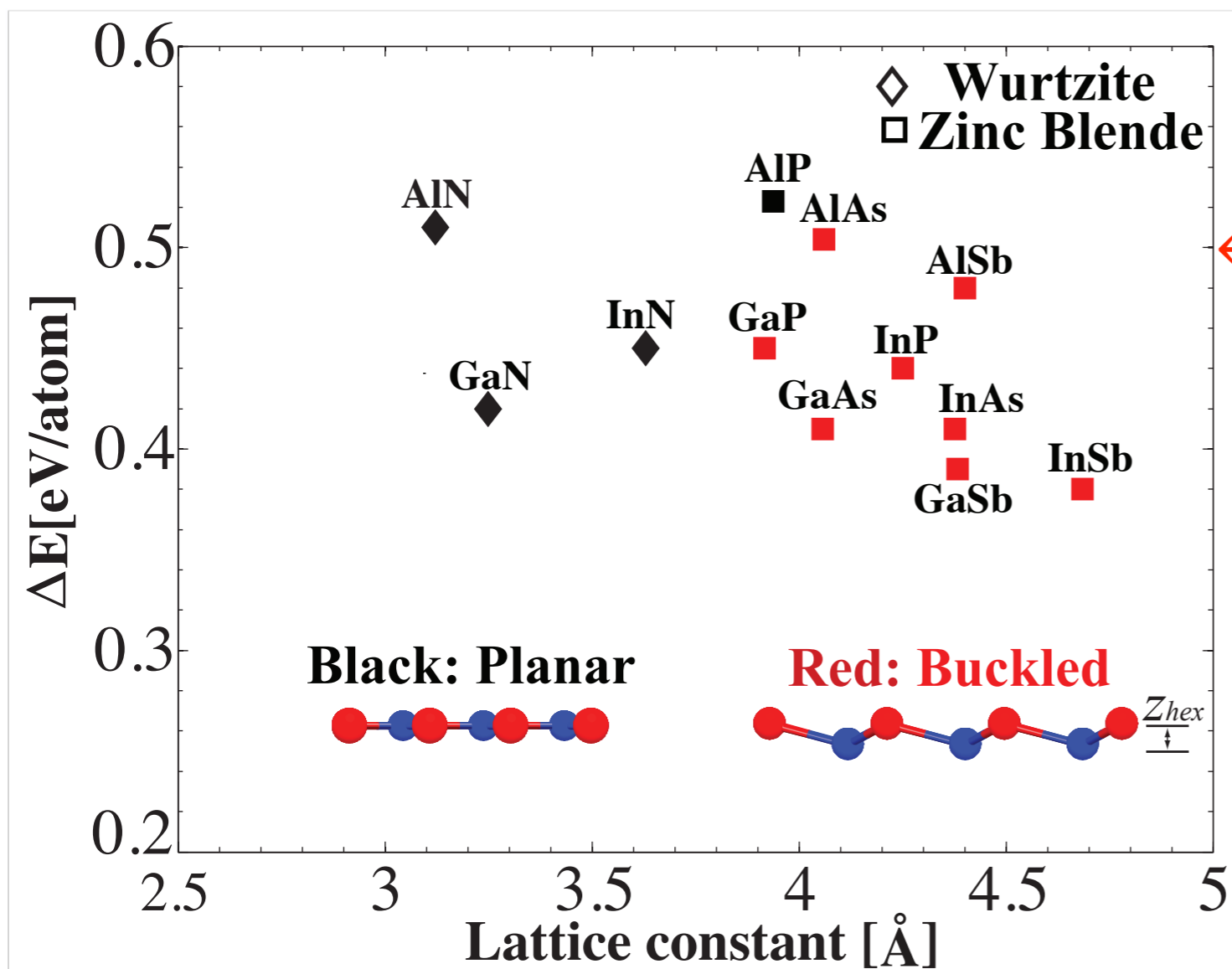
**Houlong Zhuang, Arunima Singh, Richard G. Hennig**



# Stability of 2D III-V Materials



Need to consider: Energetic and dynamic stability



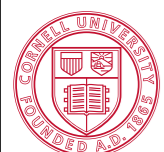
- Consider hexagonal planar and buckled III-V compounds

← SiC

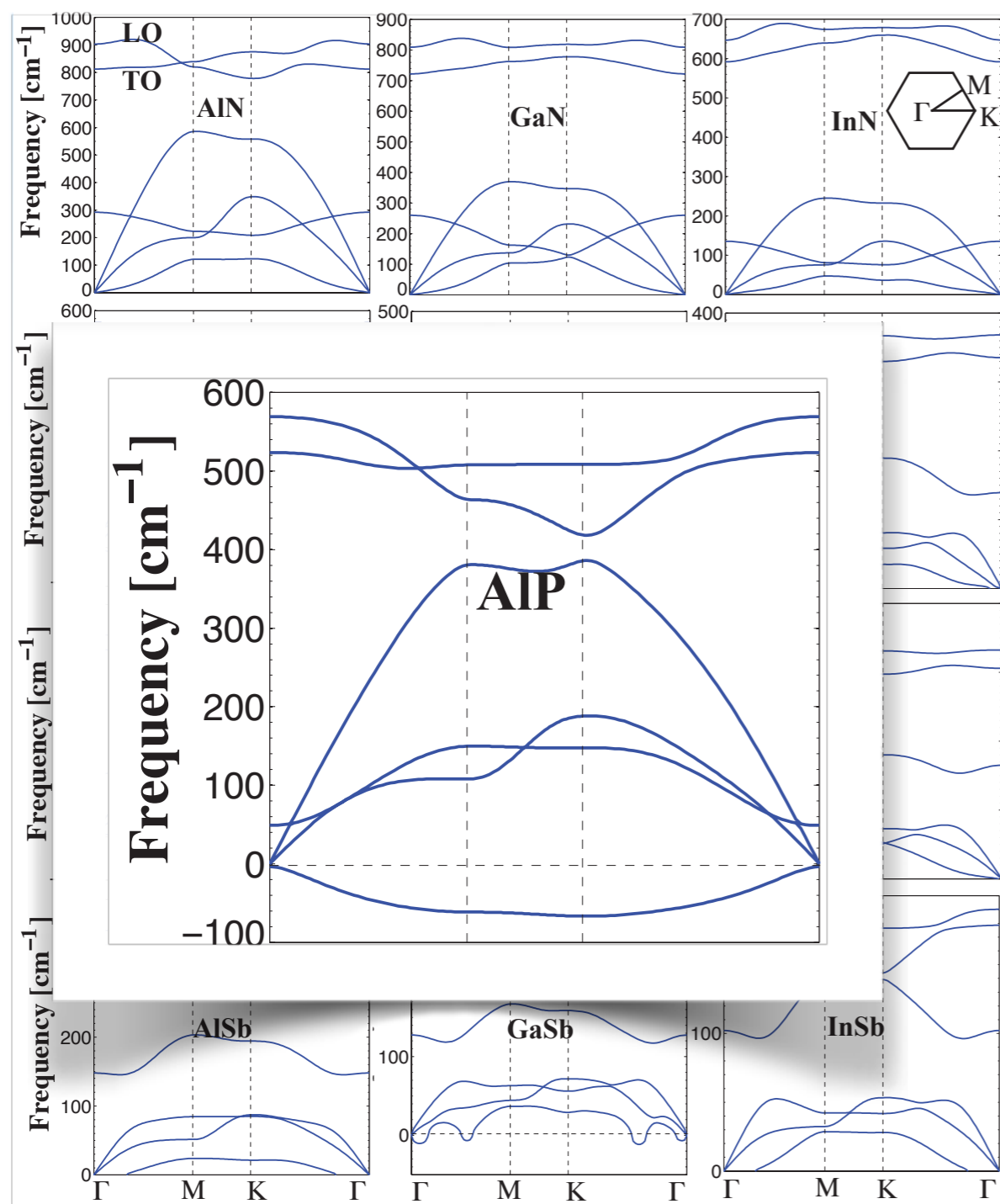
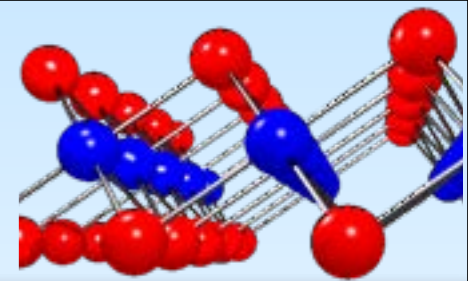
- Determine energetic stability relative to 3D bulk phase

$$\Delta E = E_{2D} - E_{3D}$$

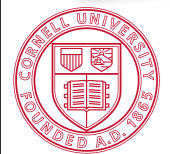
**2D hexagonal structures comparable in formation energy to SiC**



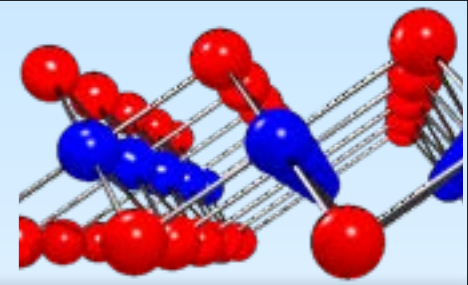
# Dynamic Stability of 2D III-V Materials



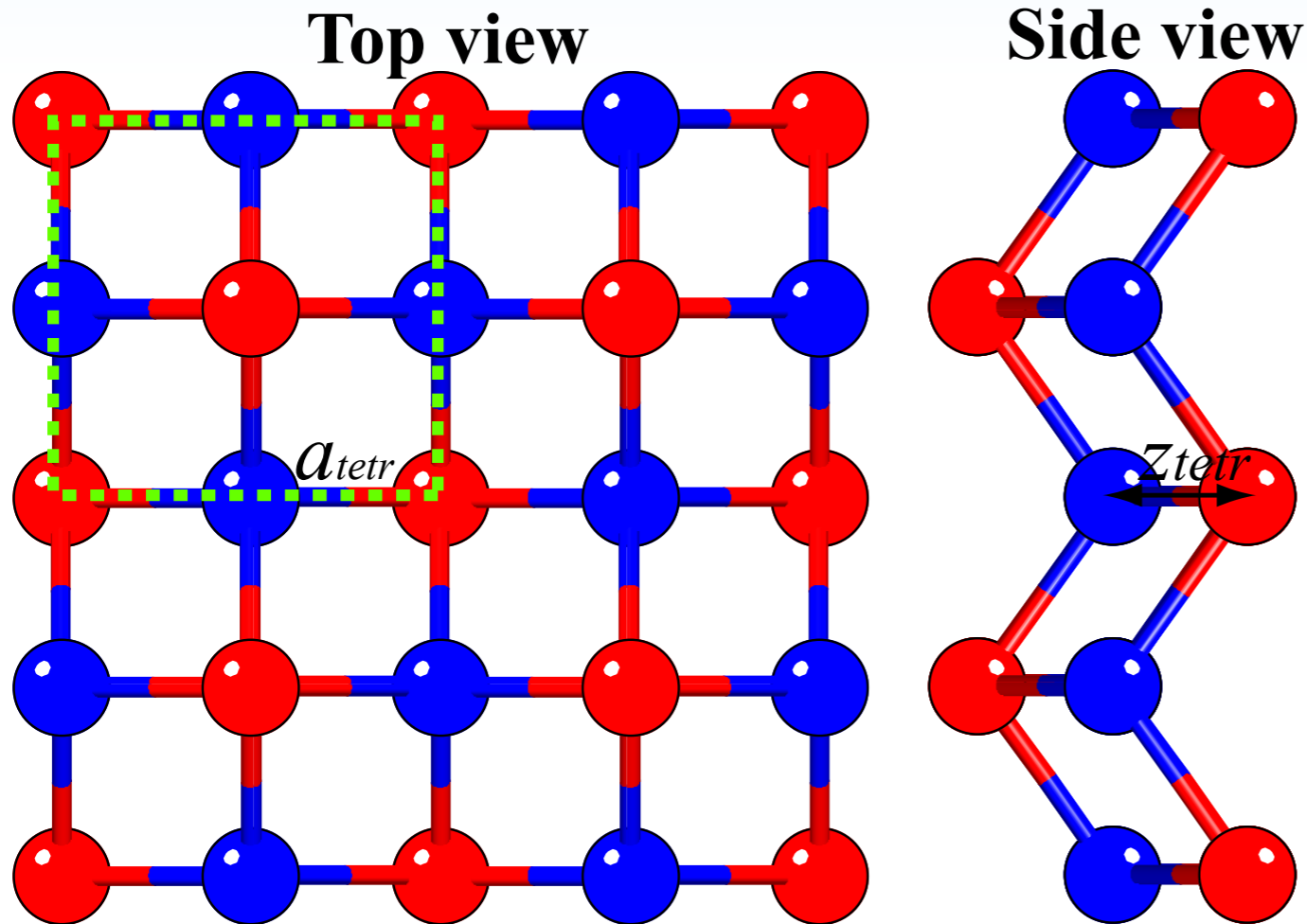
- Determine dynamic stability from phonon calculations
- Unstable phonon branches due to competition between covalent bonding preferring non-planar structures and dipole moment across buckled 2D hexagonal structure
- Remove dipole moment by looking at different reconstructions



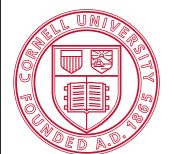
# Novel Reconstruction



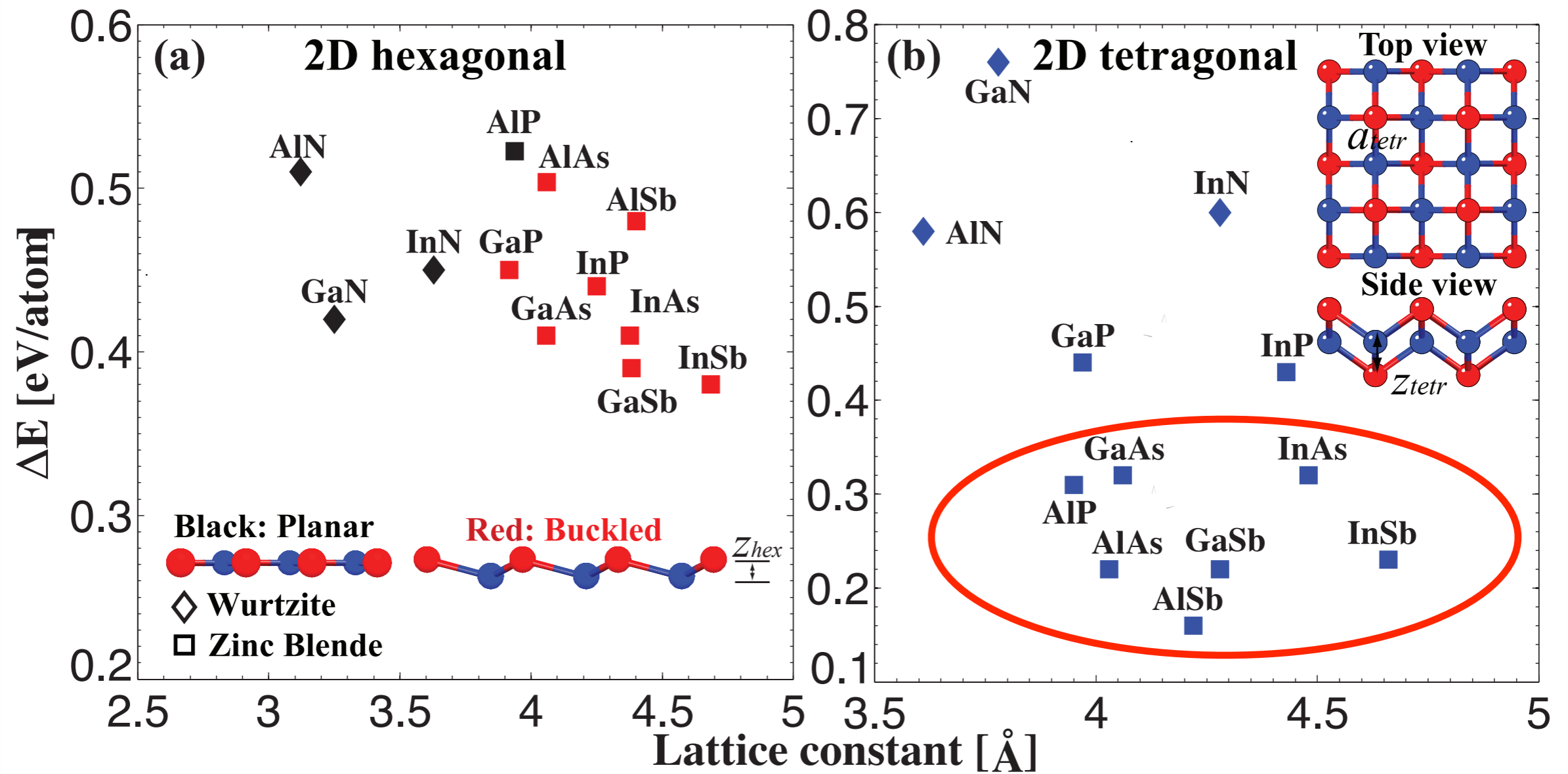
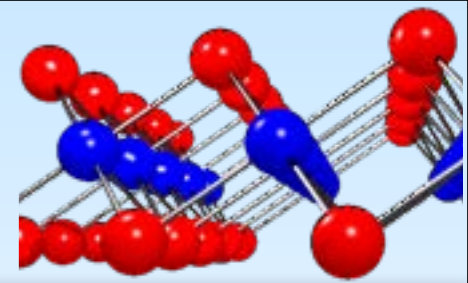
- Displace cation-anion pairs perpendicular to 2D layer
- Relaxation leads to novel dynamically stable tetragonal reconstruction
- Each group III and V element is bonded to **four** neighbors



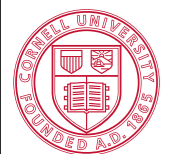
- Group III:  $sp^3$  configuration
- Group V:  $p_x, p_y$  configuration



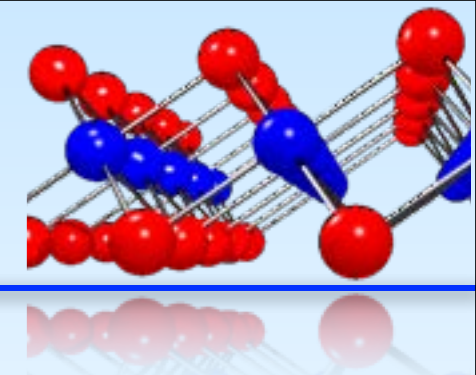
# Energetic Stability of 2D Structures



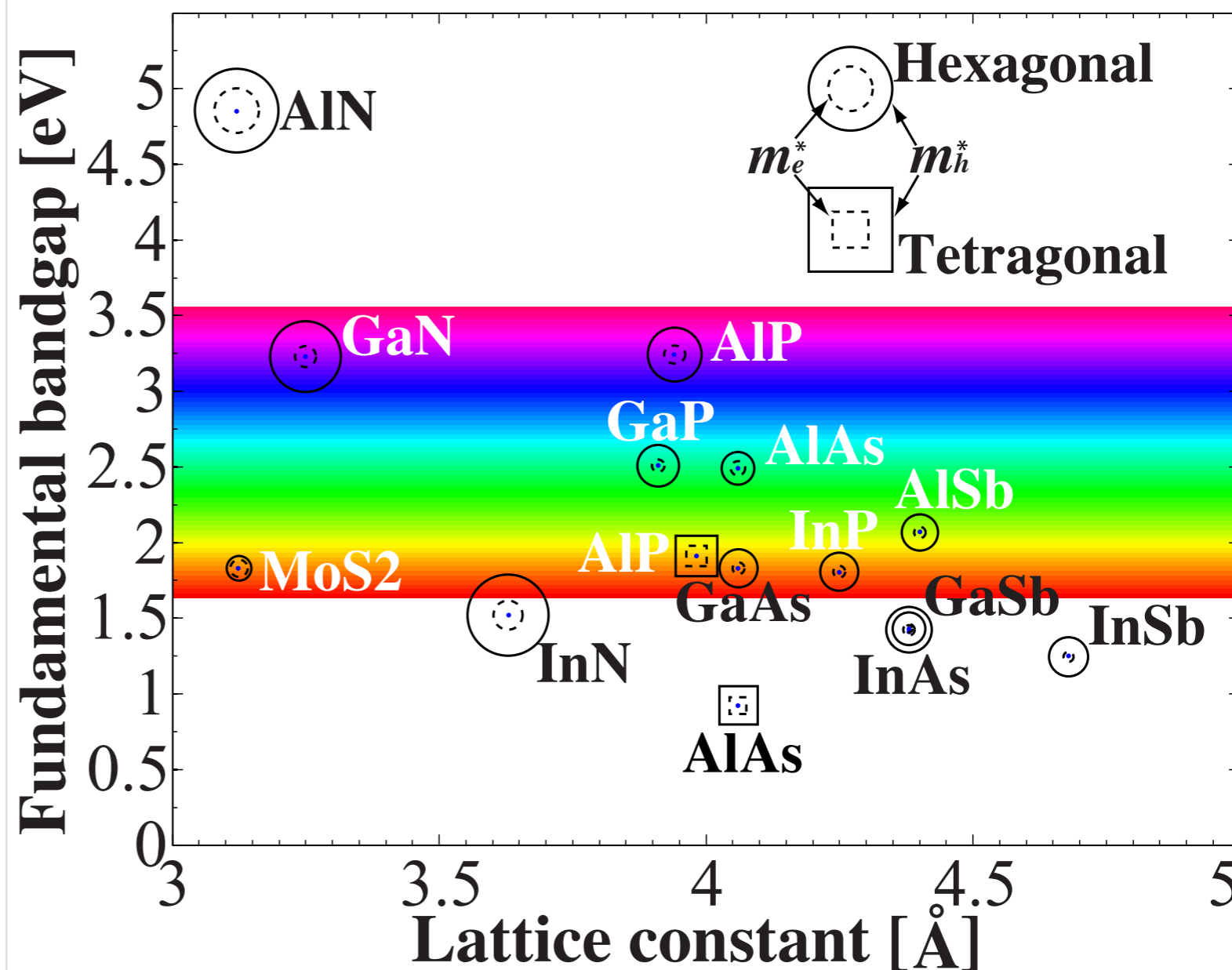
Some 2D tetragonal materials are significantly lower in energy than 2D hexagonal ones



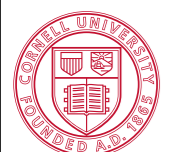
# Electronic Structure of 2D Materials



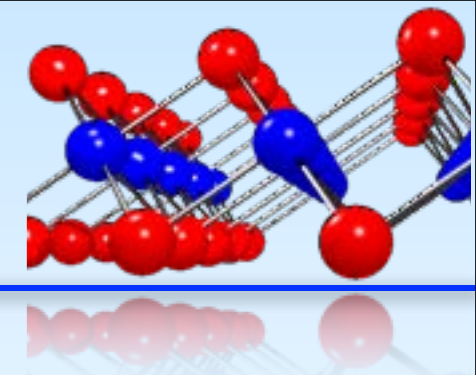
- HSE06 calculations to avoid DFT bandgap problem
- Bandgap in visible range
- Competitive effective masses
- 2D tetragonal AlP indirect gap of 1.9 eV, AlAs direct gap of 0.8 eV
- Effective electron masses of 0.5 and 0.4  $m_e$
- Comparable to MoS<sub>2</sub> 1.7 eV, 0.5  $m_e$



Phys. Rev. B 87, 165415 (2013)

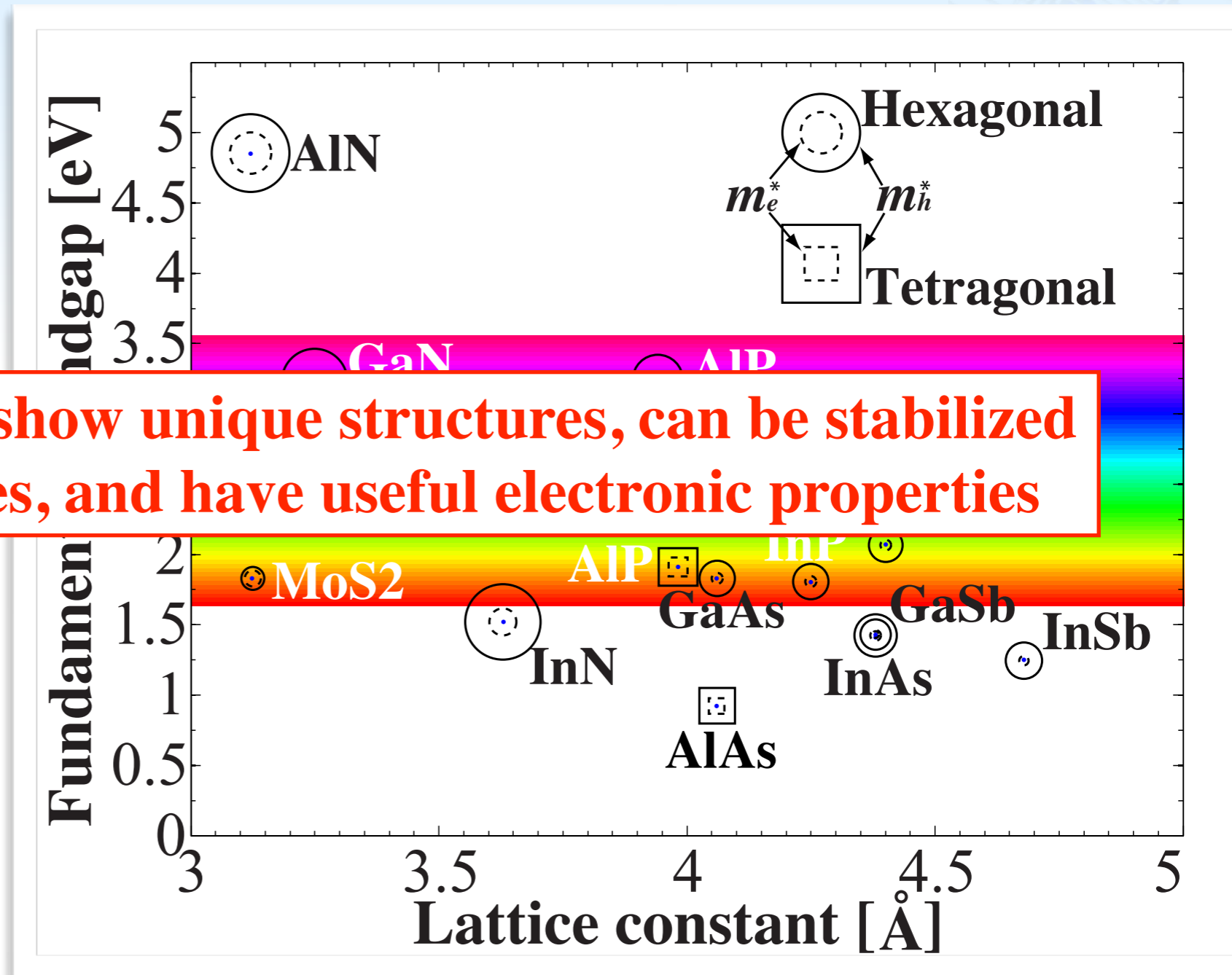


# Electronic Structure of 2D Materials

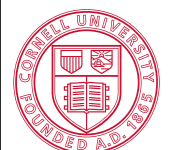


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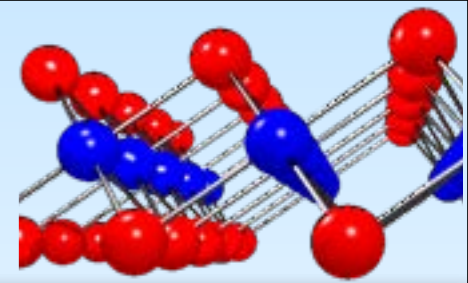
**2D III-V materials show unique structures, can be stabilized on metal substrates, and have useful electronic properties**



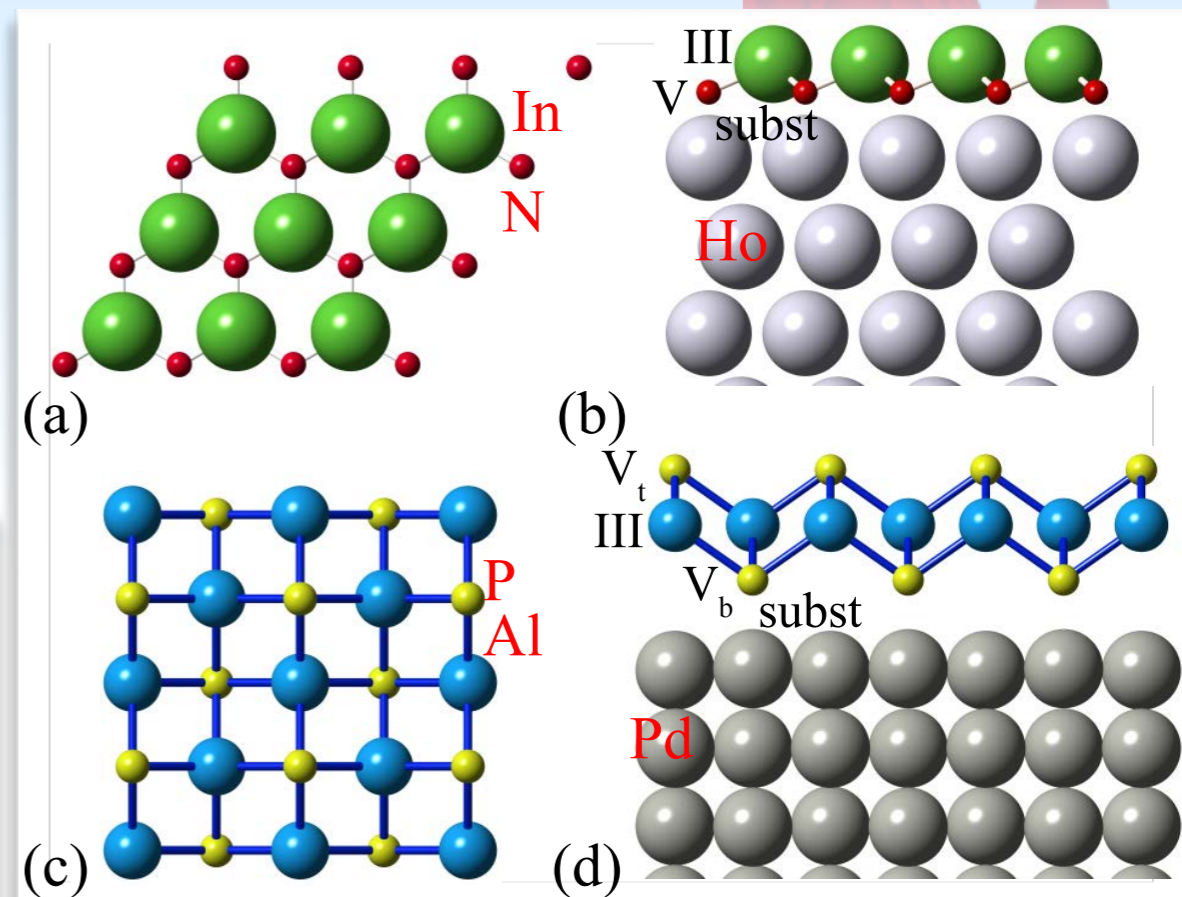
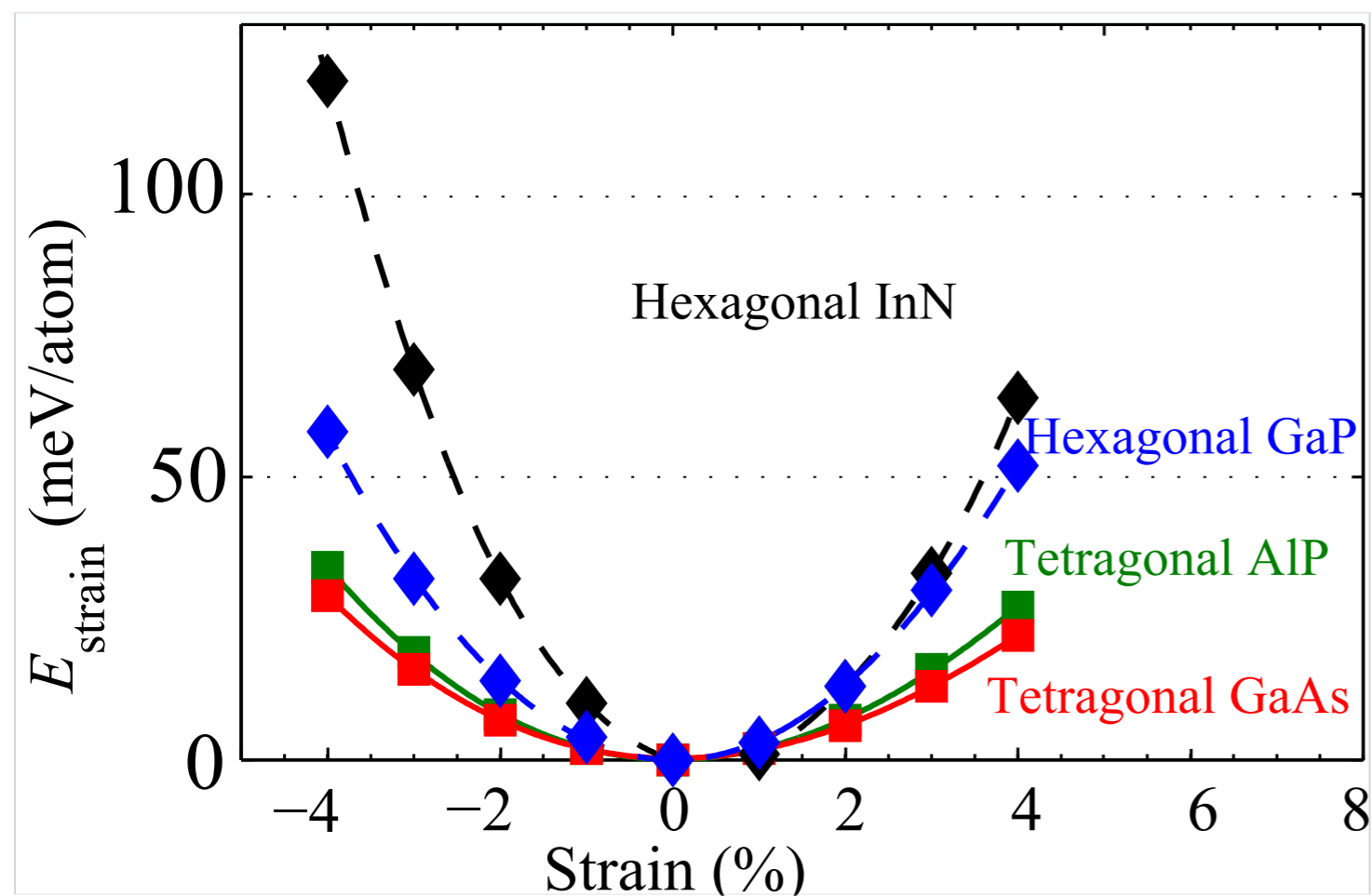
Phys. Rev. B 87, 165415 (2013)



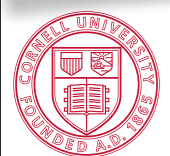
# Virtual Synthesis of 2D Materials



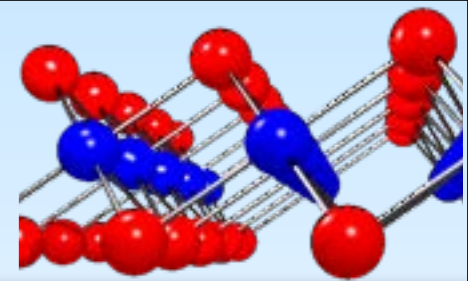
- Find lattice matched substrates
  - 2D tetragonal: (100) fcc surface
  - 2D hexagonal: (0001) hcp surface
- Balance of stabilization and strain energy



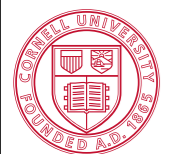
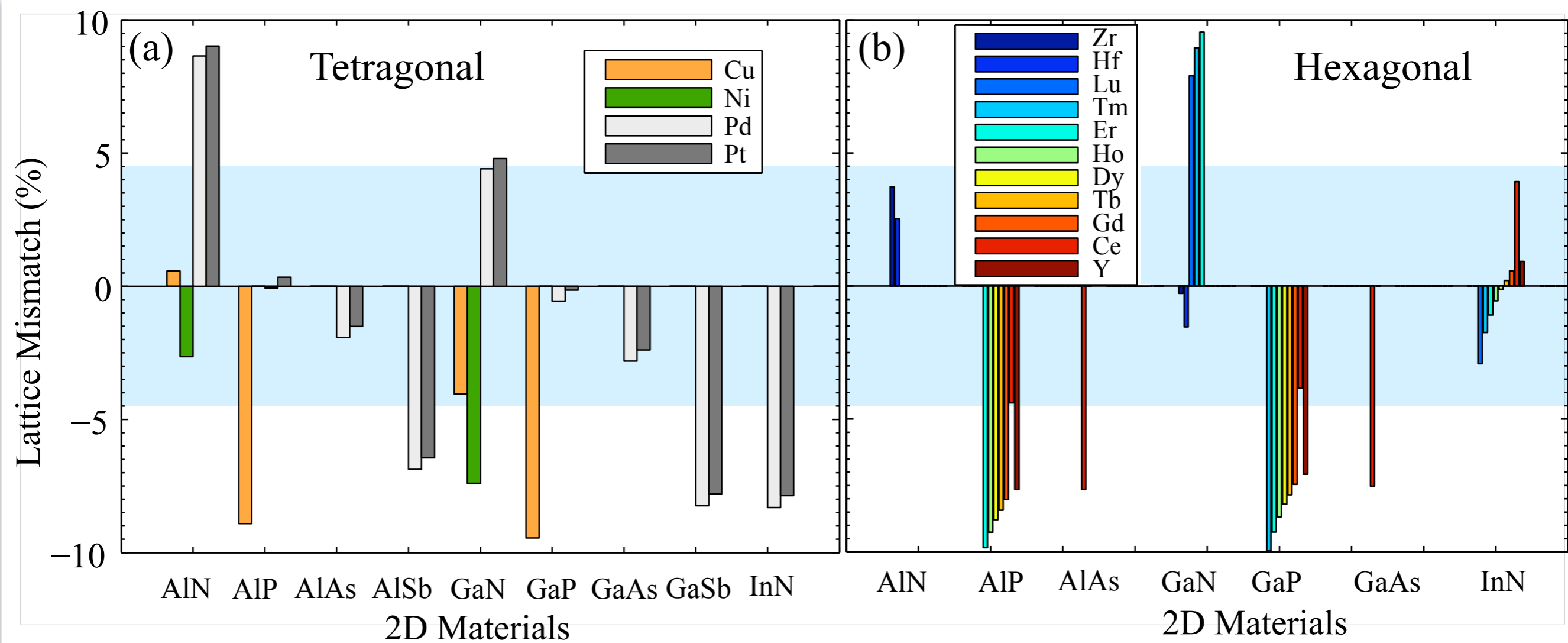
**Estimate maximum epitaxial strain of 4% to stabilize 2D materials**



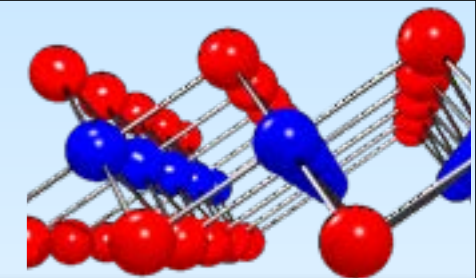
# Epitaxial Stabilization on Substrates



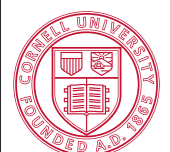
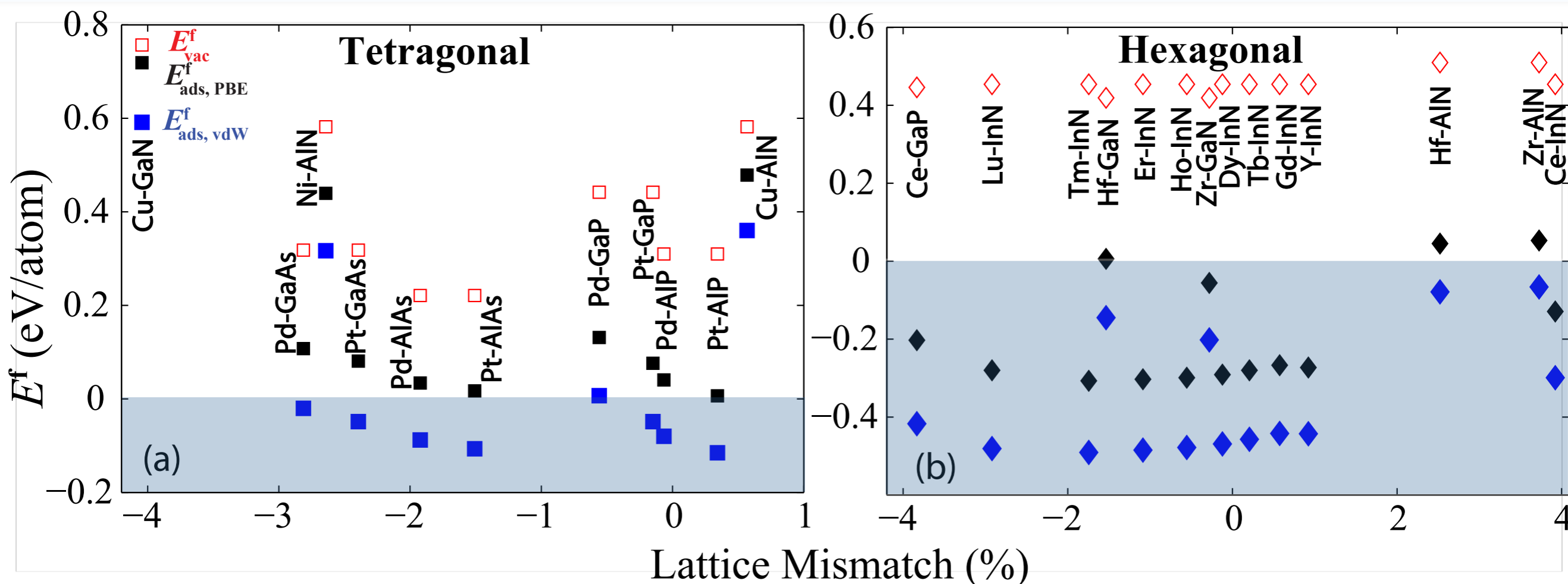
- Search ICSD for lattice matched (100) fcc and (0001) hcp surfaces
- Lattice match for **transition metal** fcc and hcp and **rare-earth metal** hcp



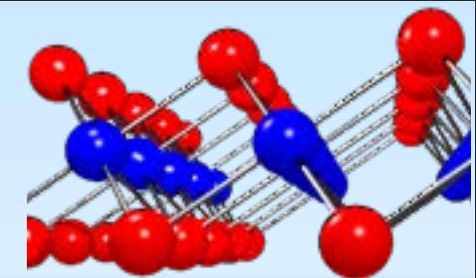
# Adsorption Energy on Substrates



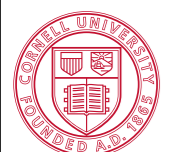
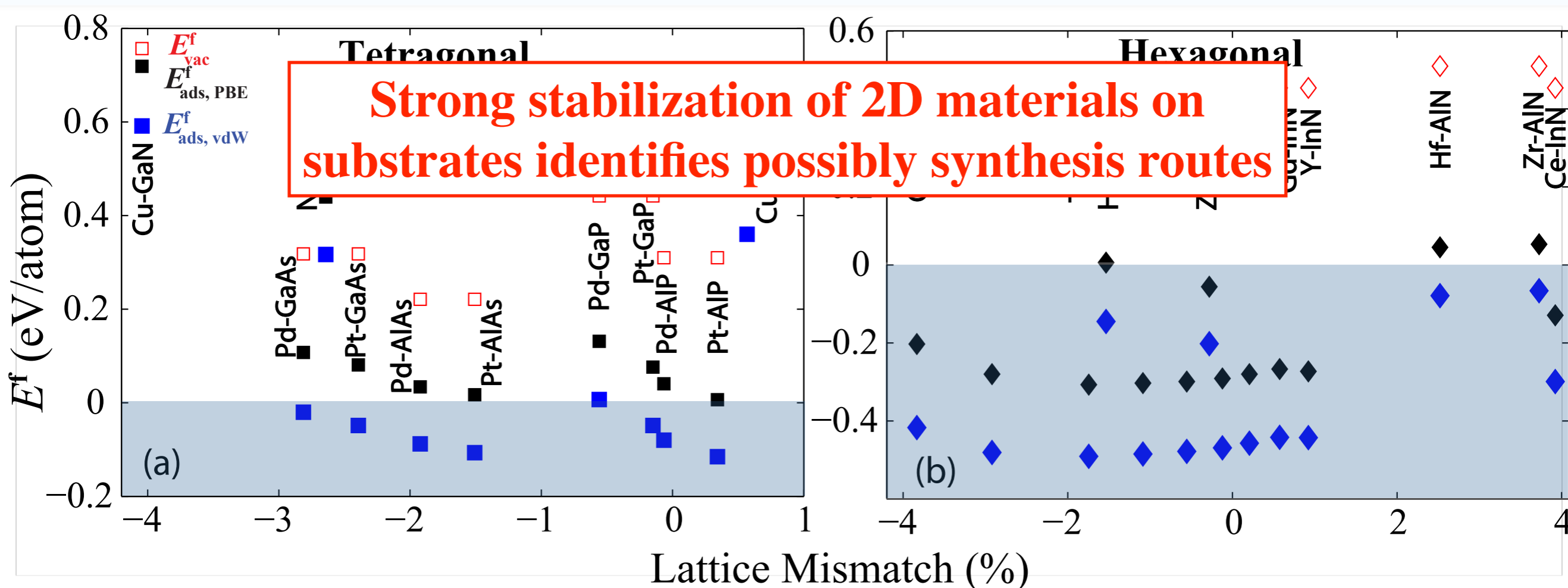
- PBE shows strong chemisorption, van der Waals interaction enhance adsorption
- Stabilization of AlP on Pd: 2D tetragonal
  - ⇒ chemisorption on Pd 0.31 eV/atom
  - ⇒ van der Waals -0.08 eV/atom



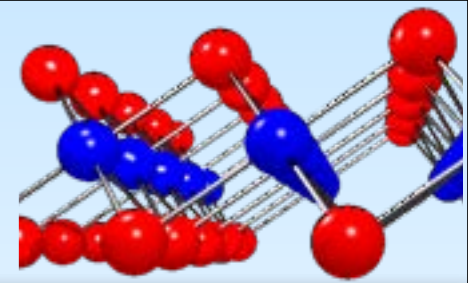
# Adsorption Energy on Substrates



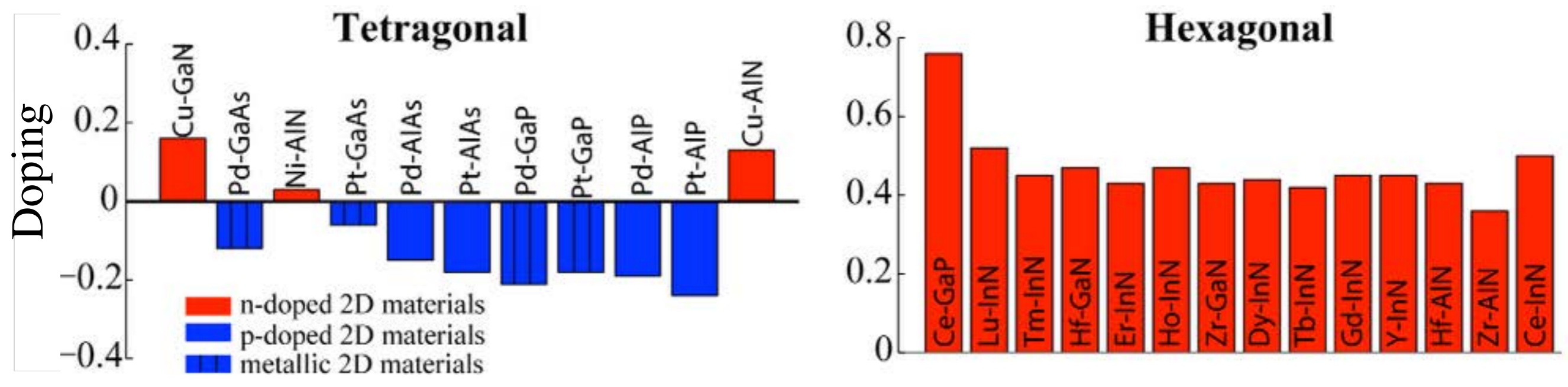
- PBE shows strong chemisorption, van der Waals interaction enhance adsorption
- Stabilization of AlP on Pd: 2D tetragonal
  - ⇒ chemisorption on Pd 0.31 eV/atom
  - ⇒ van der Waals -0.08 eV/atom



# Doping of 2D Materials by Substrate

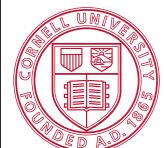


- Charge transfer between 2D material and substrate
- 2D hexagonal III-V materials are *n*-type doped
- 2D tetragonal III-V materials either *n*- or *p*-type doped



**Large adsorption energies and strong doping makes these metals good electrical contact for transport measurements and electronic applications**

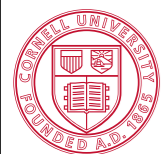
APL 101, 153109 (2012), PRB 87, 184114 (2013)



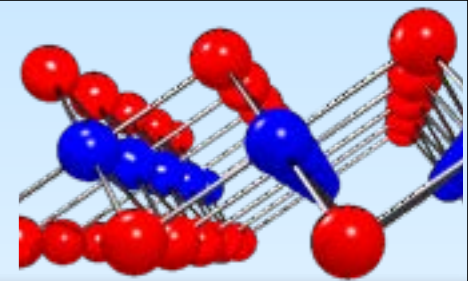
# **Discovery of 2D Materials for Photocatalytic Water Splitting**

## **Metal Dichalcogenides**

**Houlong Zhuang, Richard G. Hennig**

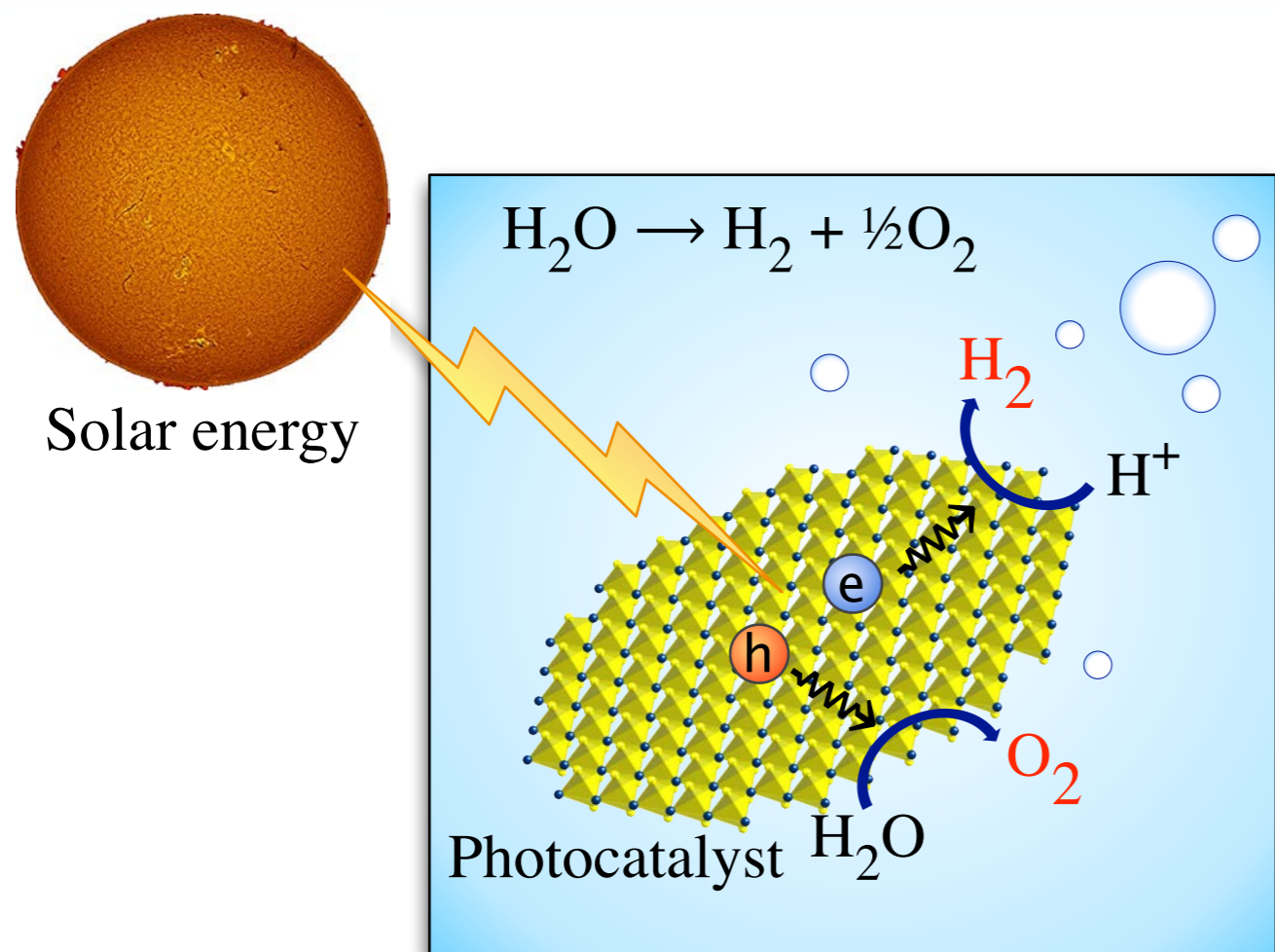


# 2D Materials for Energy Conversion

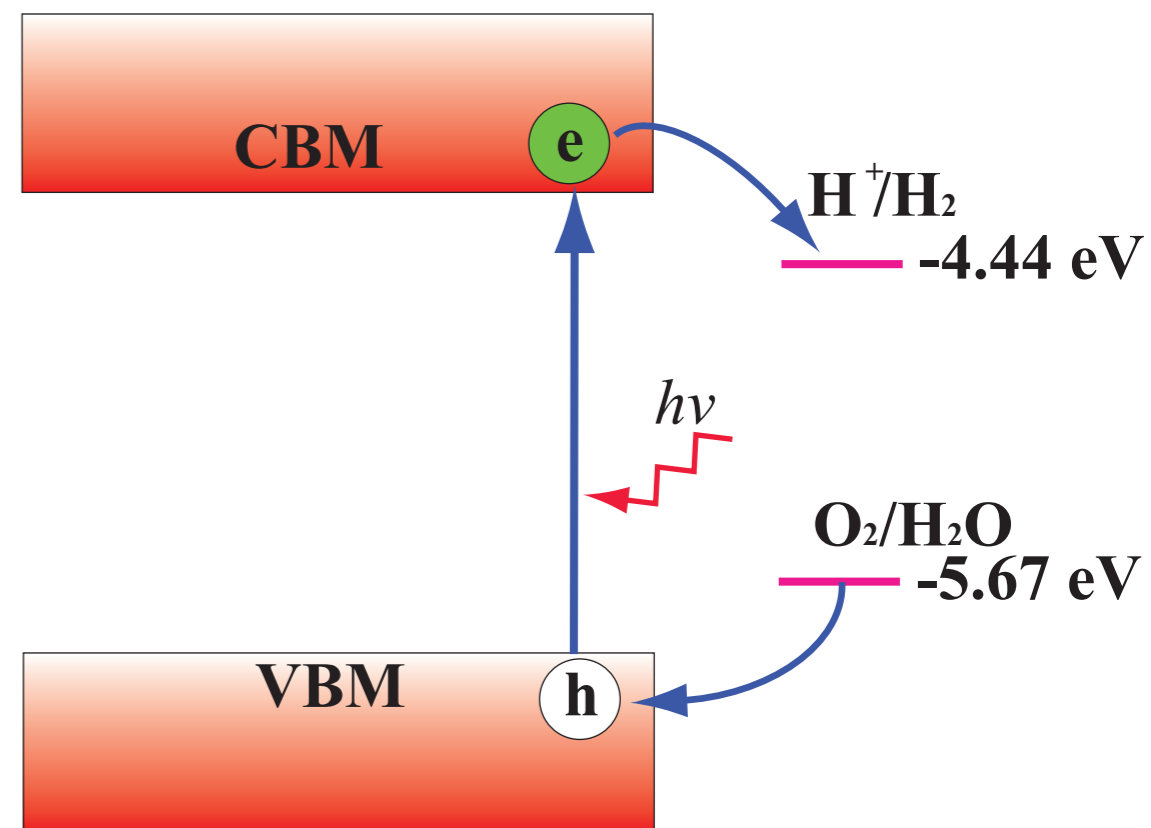


## Photocatalytic water splitting

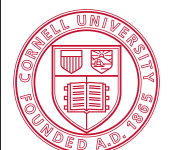
- Bandgap between 1.4 eV and 3 eV
- Band alignment with  $\text{H}^+/\text{H}_2$  and  $\text{O}_2/\text{H}_2\text{O}$  levels
- Stable in aqueous environment
- Strong optical absorption



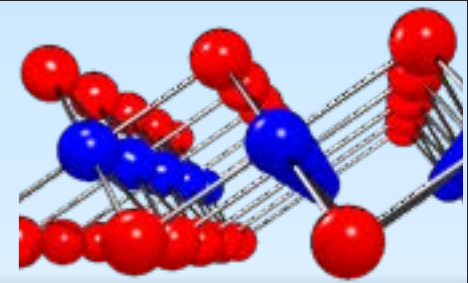
	At pH=0	At pH=7
$\text{H}^+/\text{H}_2$	-4.44 eV	-4.02 eV
$\text{O}_2/\text{H}_2\text{O}$	-5.67 eV	-5.26 eV



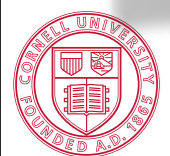
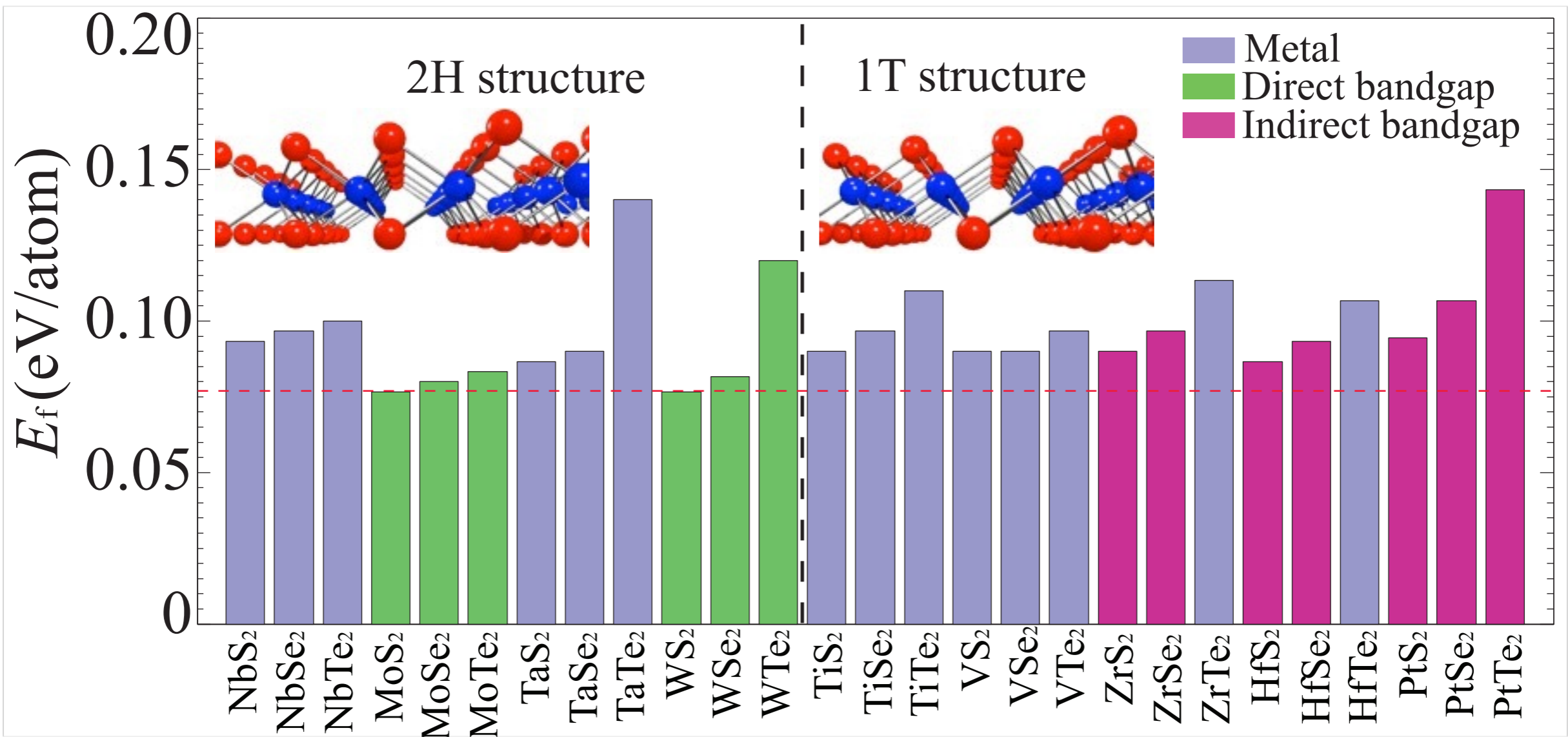
Toroker et al. Phys. Chem. Chem. Phys. 13, 16644(2011)



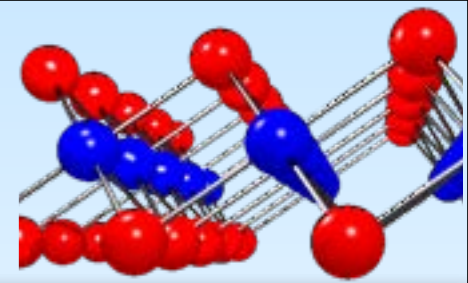
# Energetic Stability of Transition Metal Dichalcogenides



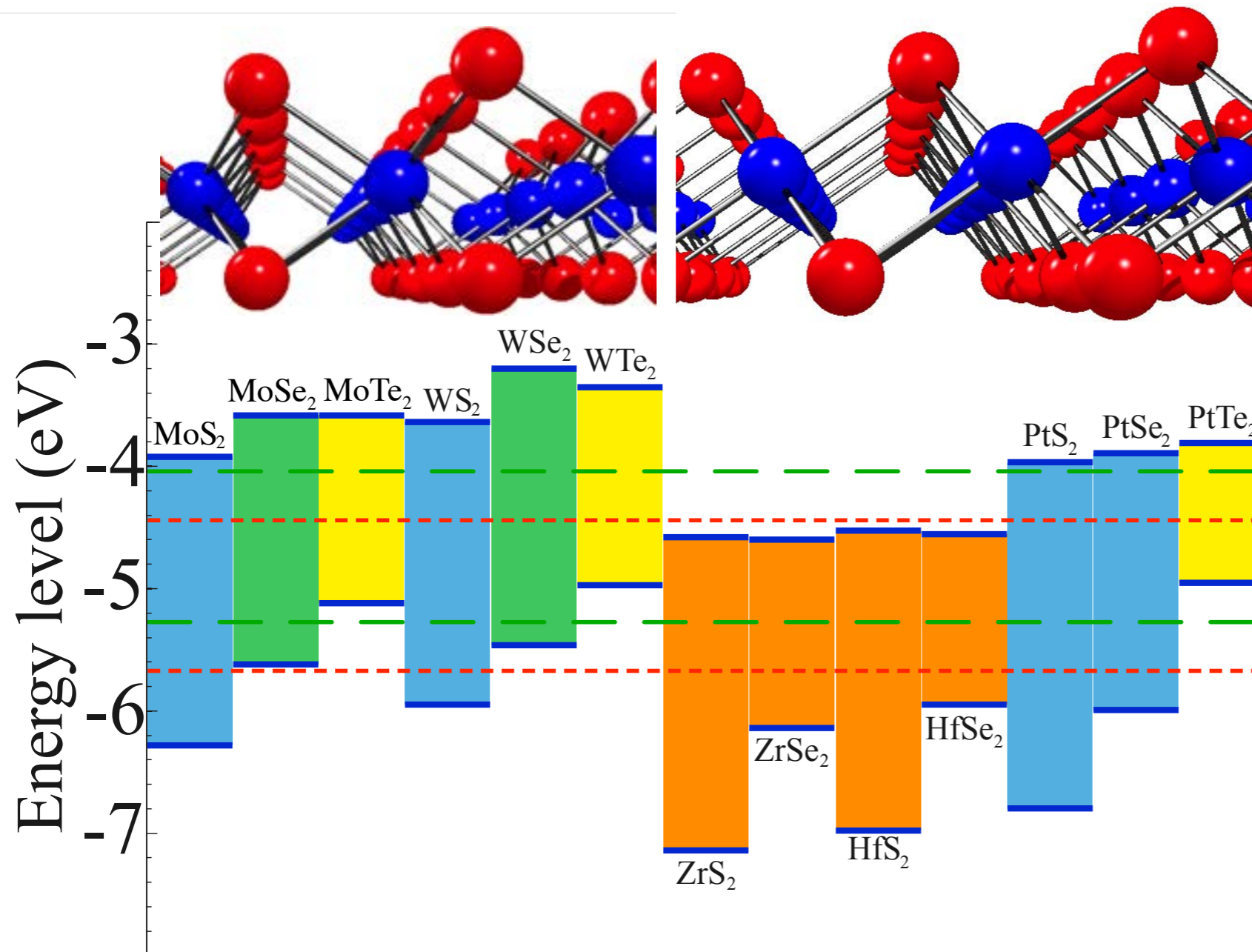
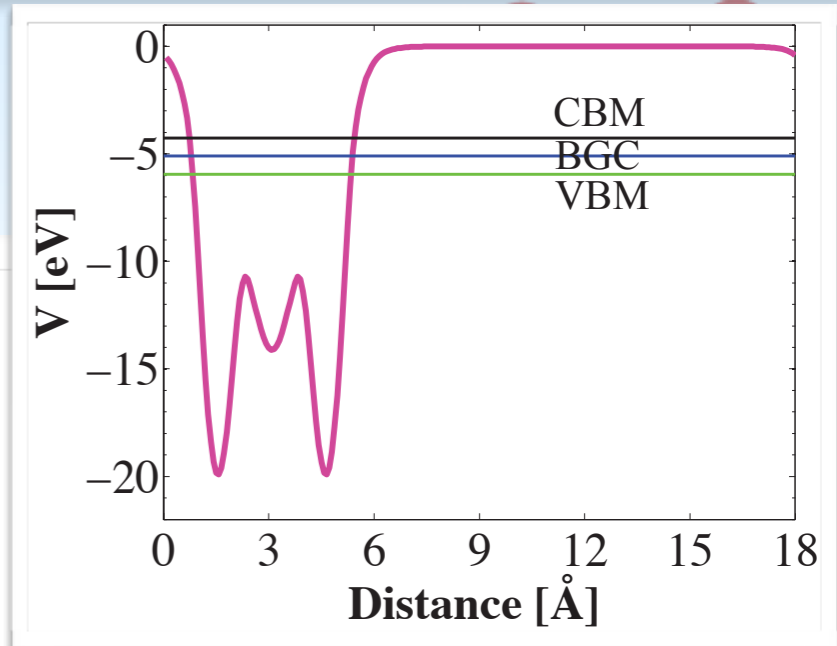
- van der Waals functional used
- Most single-layer  $\text{MX}_2$  have comparable formation energies to  $\text{MoS}_2$
- 13 out of 27  $\text{MX}_2$  are semiconductors



# Band Alignments



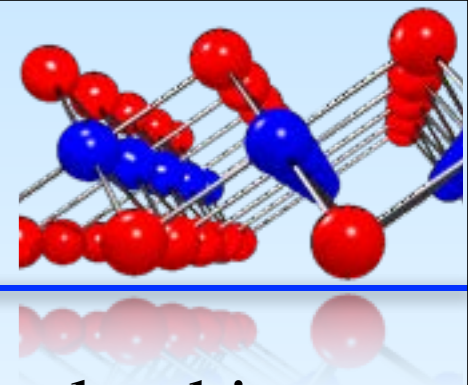
- Align the vacuum levels using PBE for bandgap center energy
- $G_0W_0$  bandgaps for CBM and VBM alignments



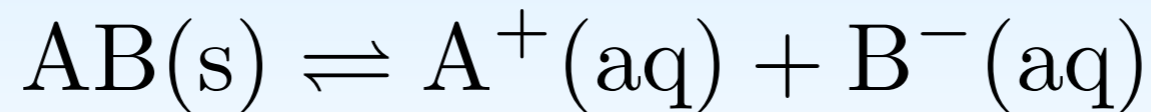
**2D MoS<sub>2</sub>, WS<sub>2</sub>, PtS<sub>2</sub>  
and PtSe<sub>2</sub> suitable  
for water splitting**



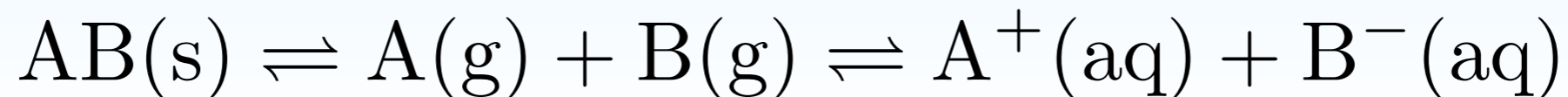
# Stability in Aqueous Solution



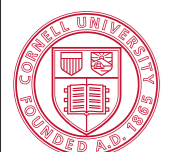
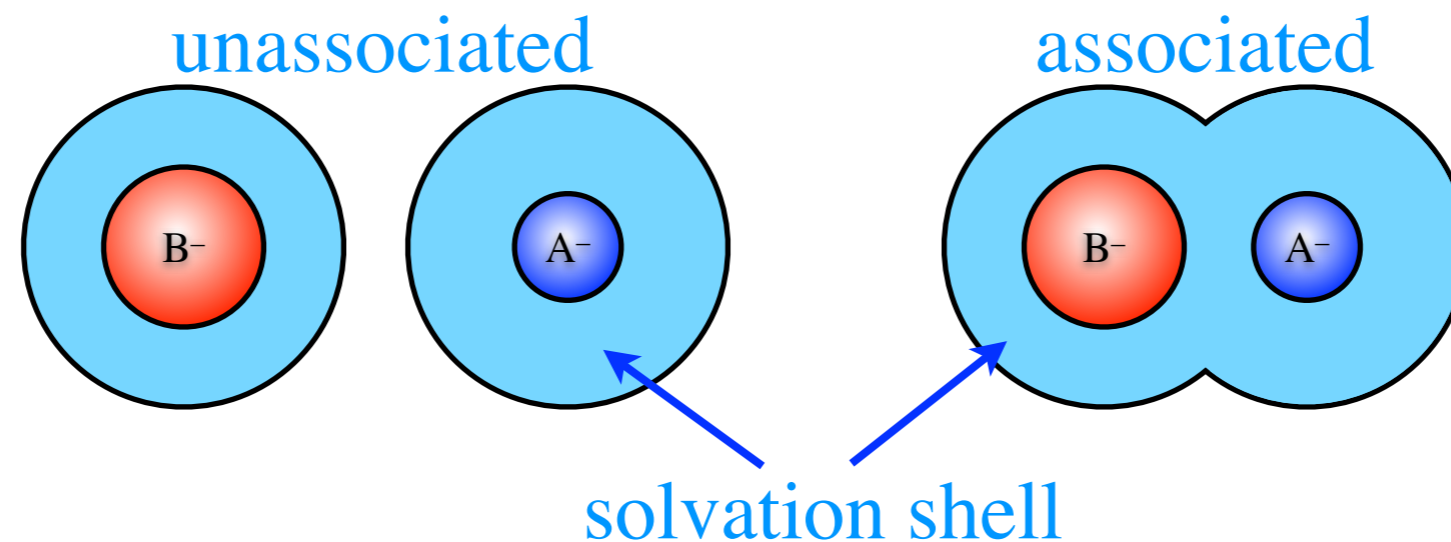
- Solubility of solid compound in water by from equilibrium with dissolved ions



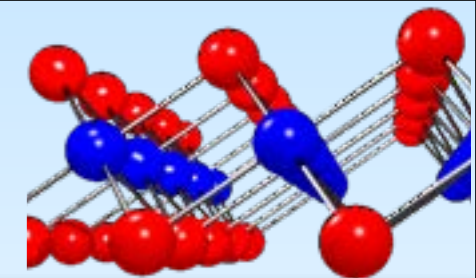
- Split reaction into two steps



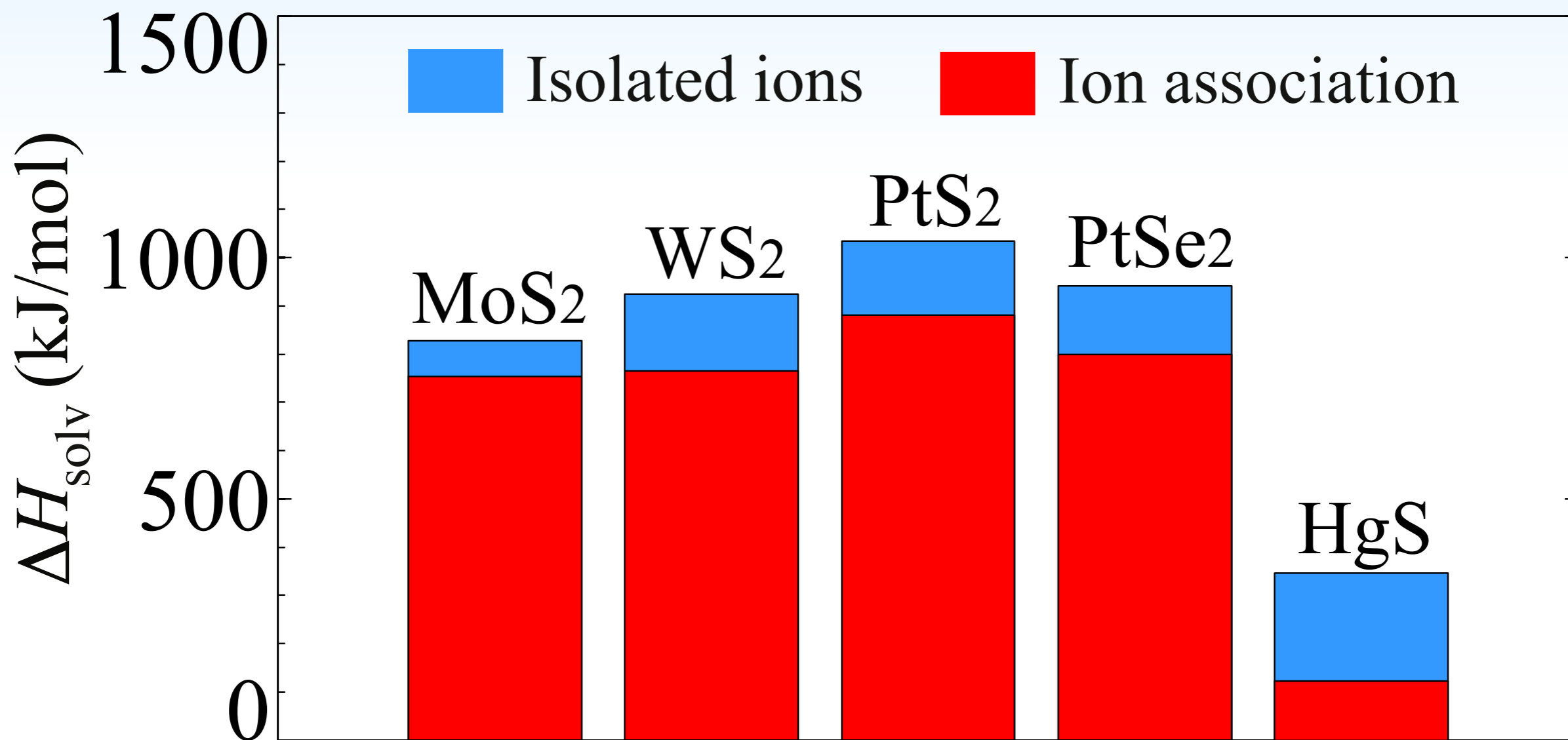
- First reaction enthalpy equals cohesive energy (calculated using VASP)
- Second reaction enthalpy given by sum of ionization and hydration enthalpy
  - Calculated with Gaussian09 (aug-cc-pVQZ basis, SMD solvation model)
  - Consider **explicit waters** and **ion association**



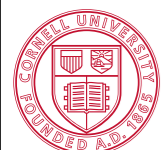
# Stability in Aqueous Solution



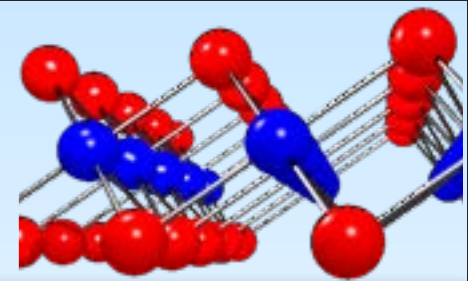
- Comparison with known poor soluble HgS shows that these materials are insoluble in water



J. Phys. Chem. C 117, 20440 (2013)



# SnS<sub>2</sub> for Photocatalytic Water Splitting



Angewandte  
International Edition  
Chemie

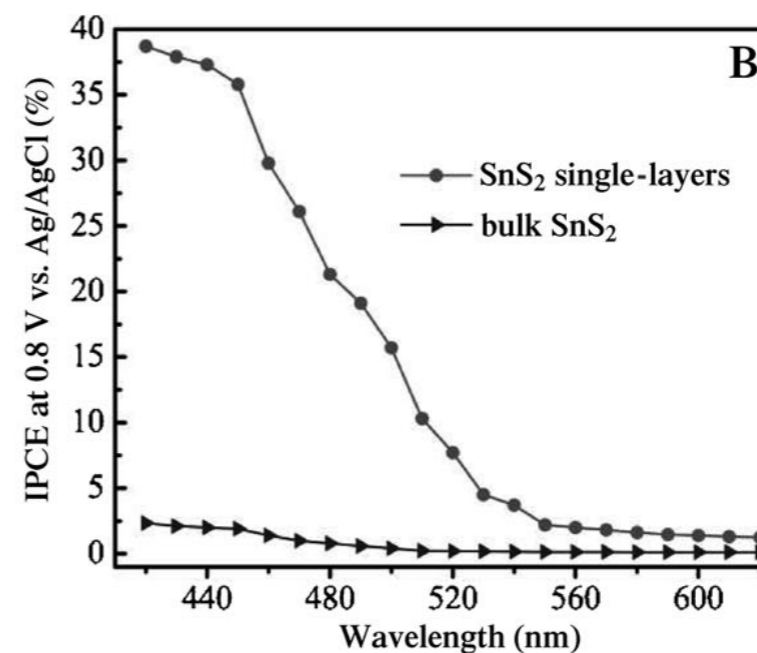
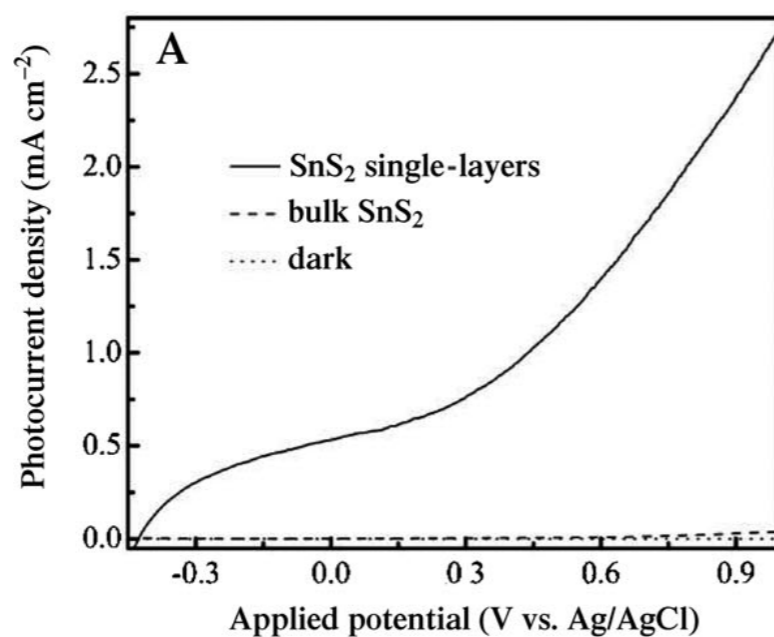
DOI: 10.1002/anie.201204675

VIP Water Splitting

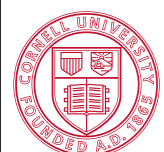


## Freestanding Tin Disulfide Single-Layers Realizing Efficient Visible-Light Water Splitting\*\*

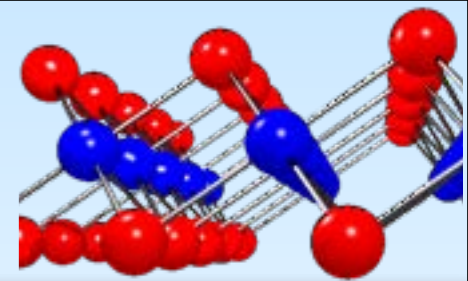
Yongfu Sun, Hao Cheng, Shan Gao, Zhihu Sun, Qinghua Liu, Qin Liu, Fengcai Lei, Tao Yao, Jingfu He, Shiqiang Wei,\* and Yi Xie\*



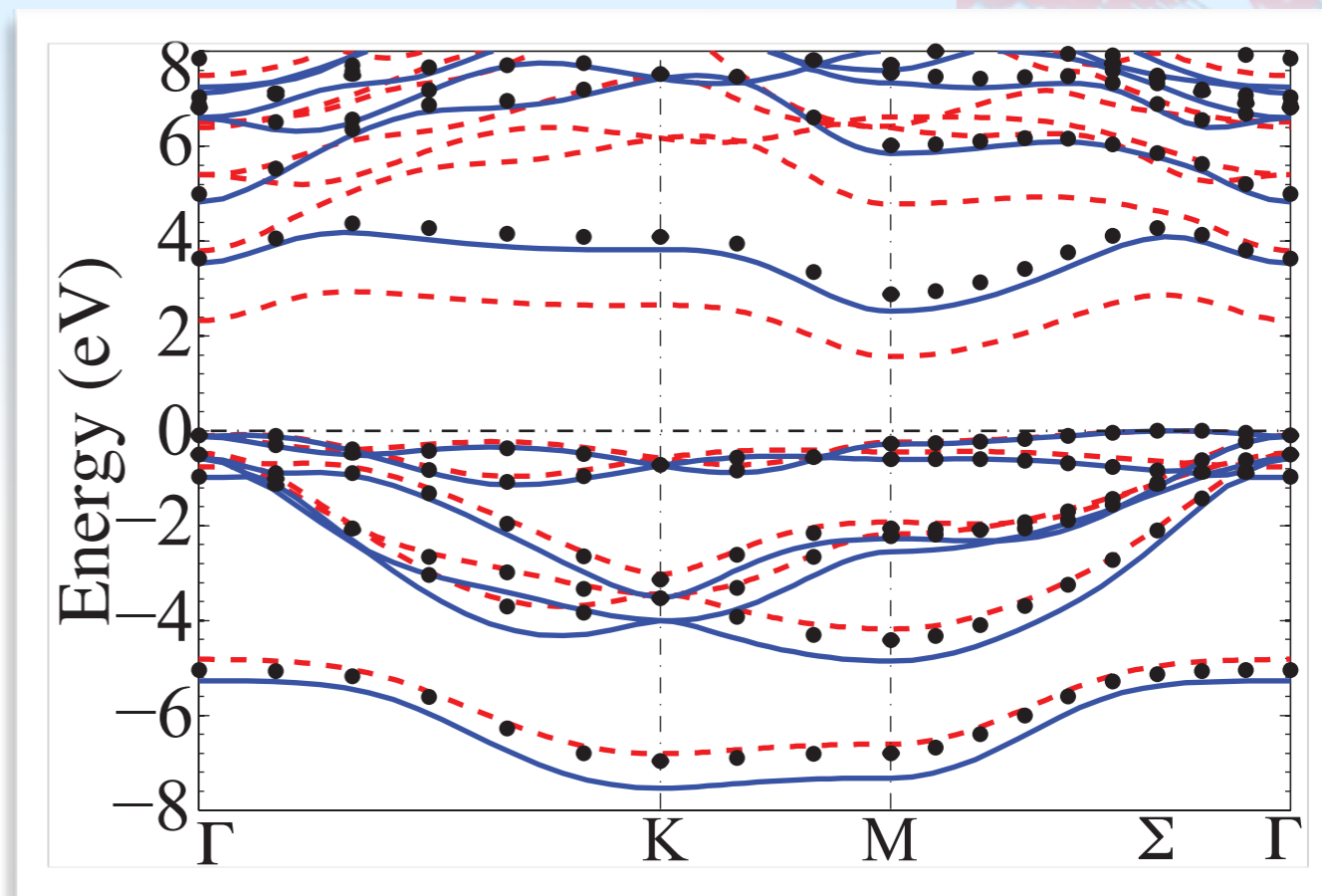
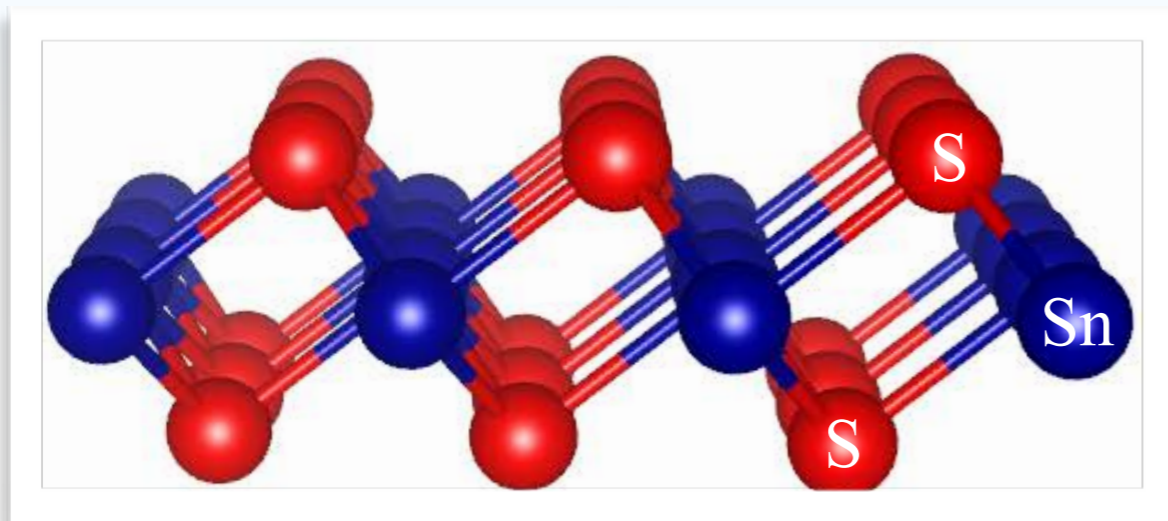
SnS<sub>2</sub> single-layers reached visible-light conversion efficiency of 38.7% at bias potential of 1 V, superior to most existing materials



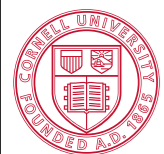
# Electronic Structure of Single-Layer SnS<sub>2</sub>



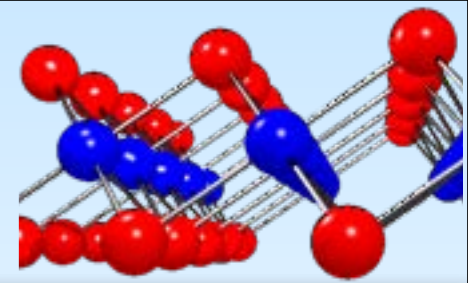
- 1T structure like PtS<sub>2</sub>
- Indirect gap, direct gap 0.3 V higher



Gap	$E_g^{\text{PBE}}$	$E_g^{\text{HSE06}}$	$E_g^{G_0W_0}$	Experiment
Indirect ( $\Sigma$ -M)	1.57	2.52	2.88	2.23
Direct (M-M)	1.81	2.81	3.16	2.55

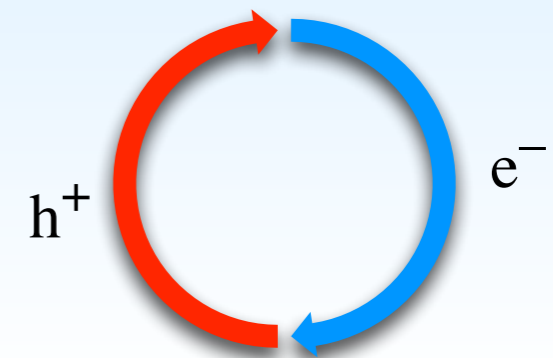


# Exciton in Single-Layer SnS<sub>2</sub>



- Many-body calculation of optical properties
- Solve **Bethe-Salpeter equation (BSE)**

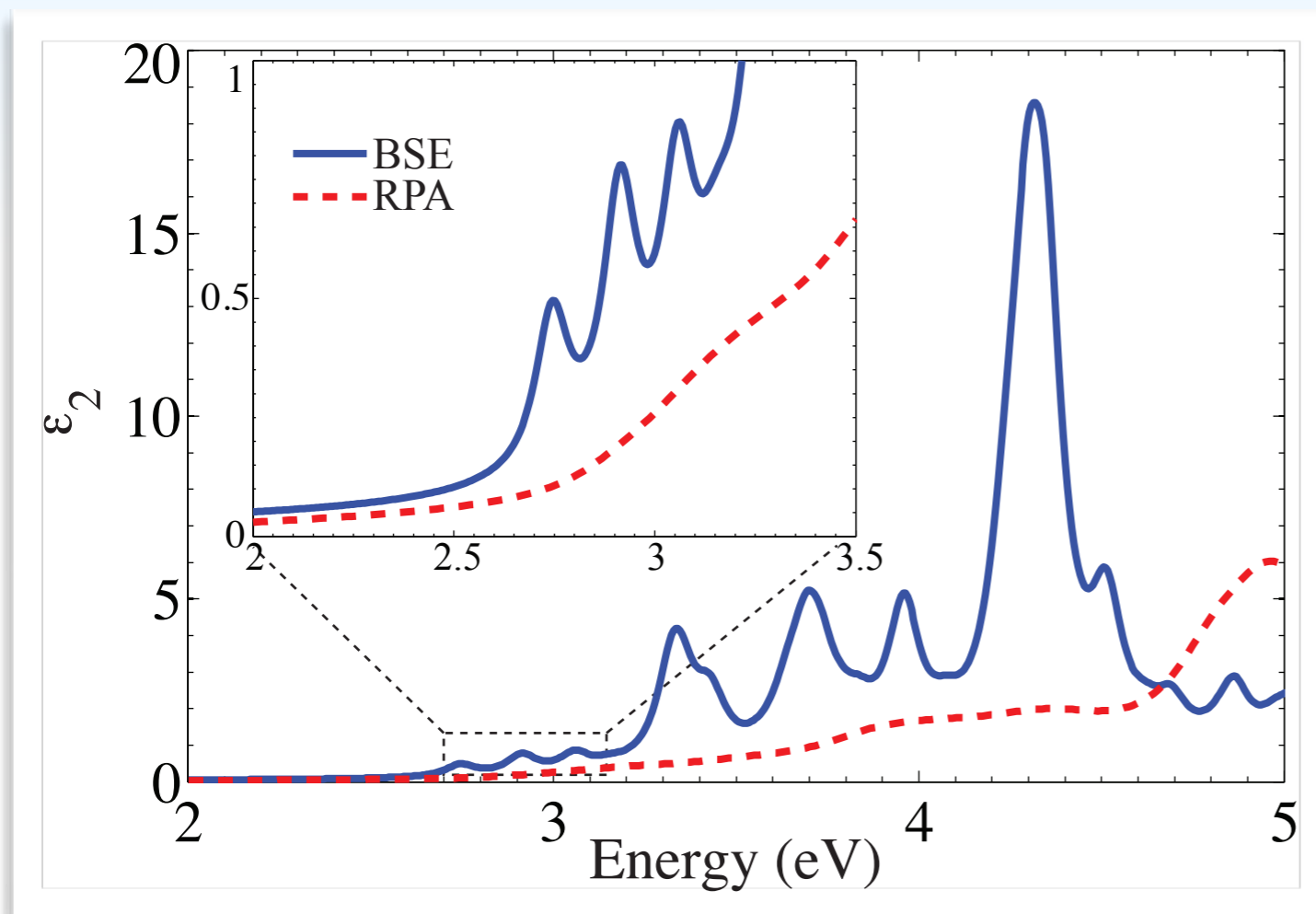
## 2D Mott-Wannier model



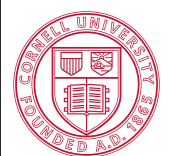
$$E_0 = 4 \frac{m_r}{m_0} \frac{R_\infty}{\epsilon_{2D}^2}$$

$$\epsilon_{2D} = \sqrt{\epsilon_{||} \cdot \epsilon_{\perp}}$$

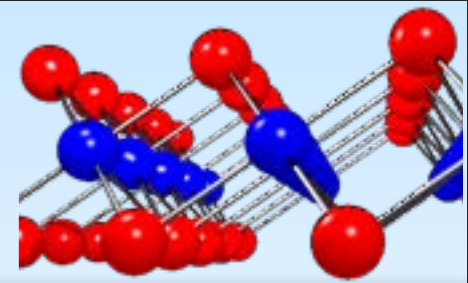
$$\frac{1}{m_r} = \frac{1}{m_e} + \frac{1}{m_h}$$



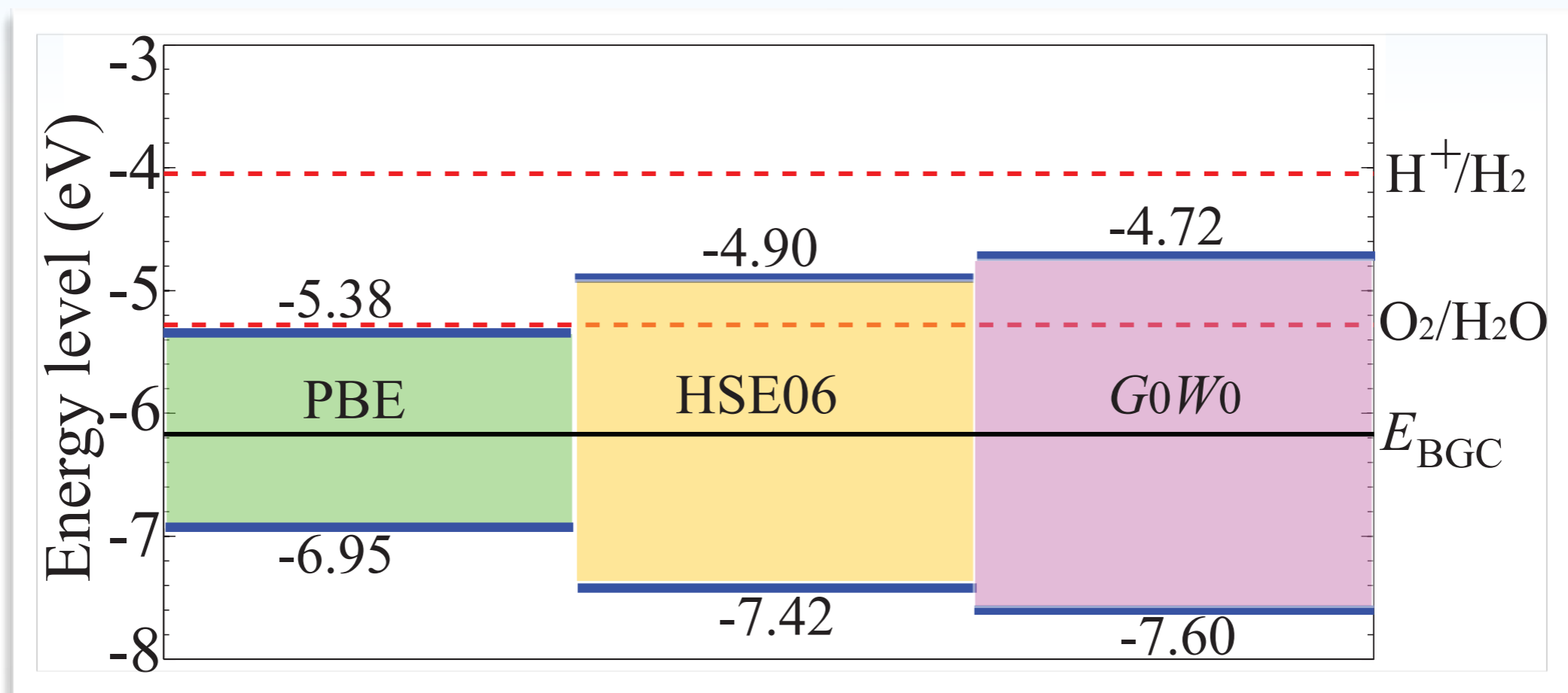
**Exciton binding energy of 0.41 eV in model and BSE**



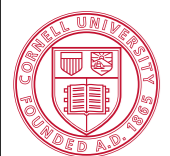
# Band Alignment for Single-Layer SnS<sub>2</sub>



- Experiment: Photocatalysis requires bias potential of 1 V, reduces efficiency
- Calculated band alignment: H<sup>+</sup>/H<sub>2</sub> evolution requires bias of > 0.9 eV
- Strain reduces required bias potential



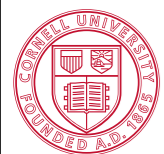
Phys. Rev. B 88, 115314 (2013)



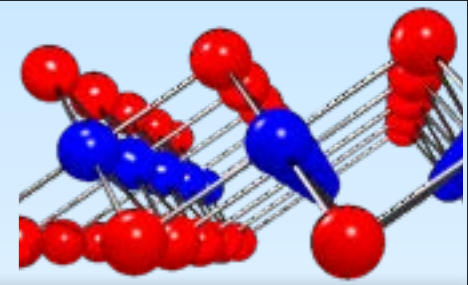
# **Discovery of 2D Materials for Photocatalytic Water Splitting**

## **Group-III Monochalcogenides**

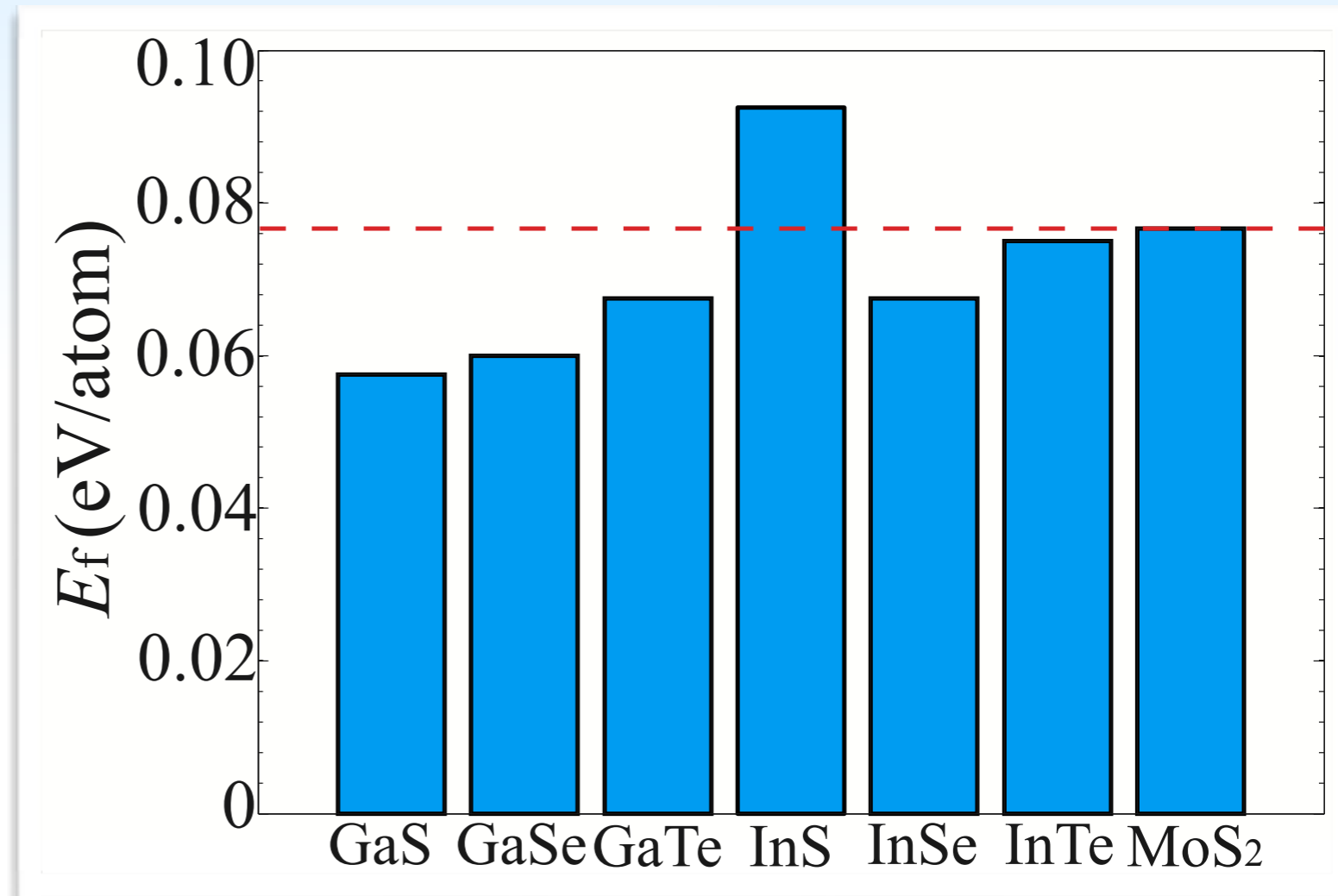
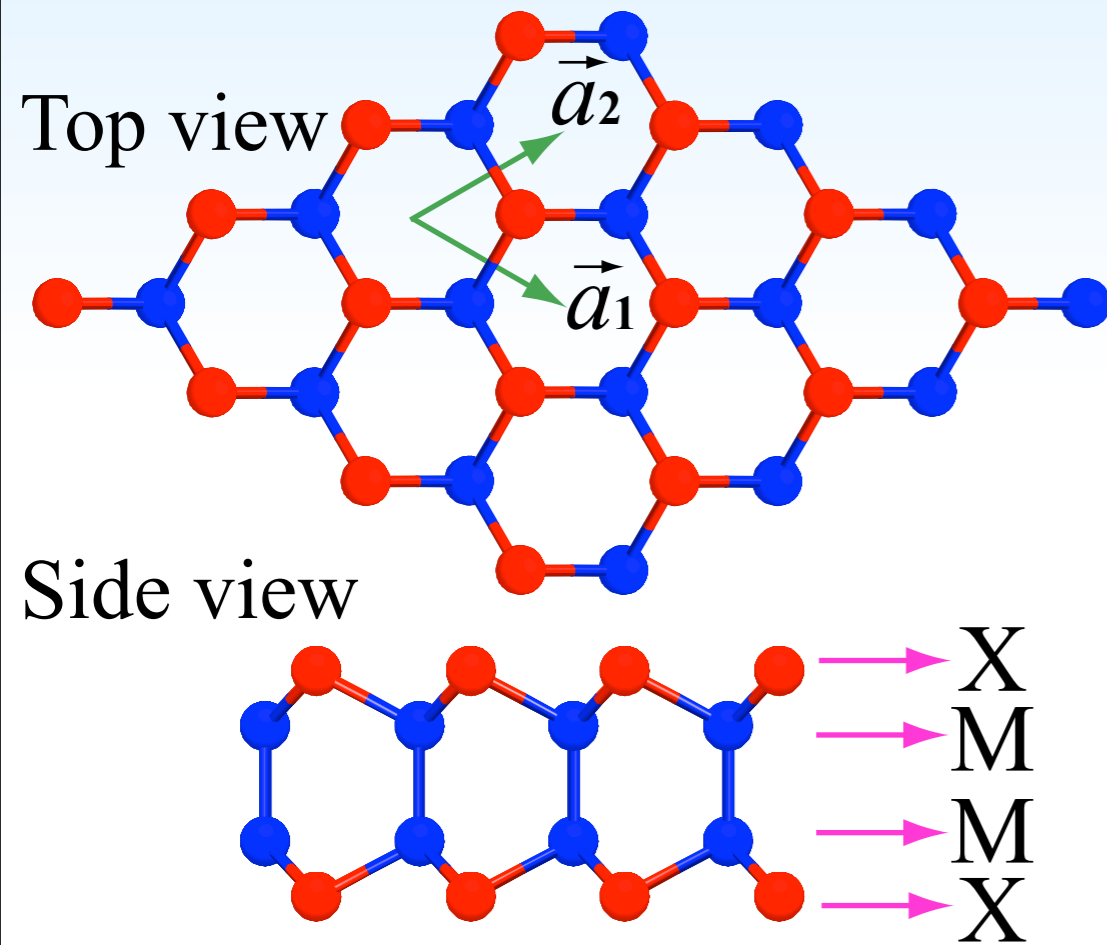
**Houlong Zhuang, Richard G. Hennig**



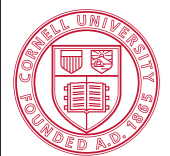
# Group-III Monochalcogenides for Water Splitting



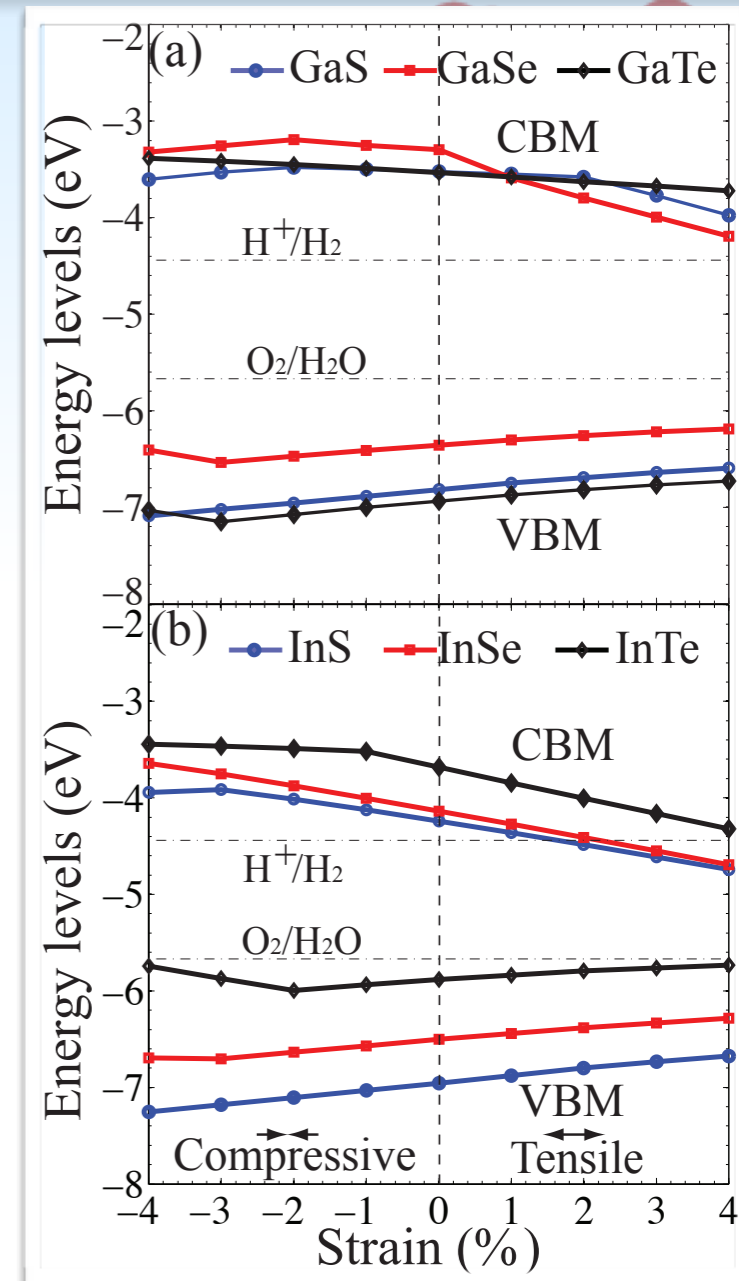
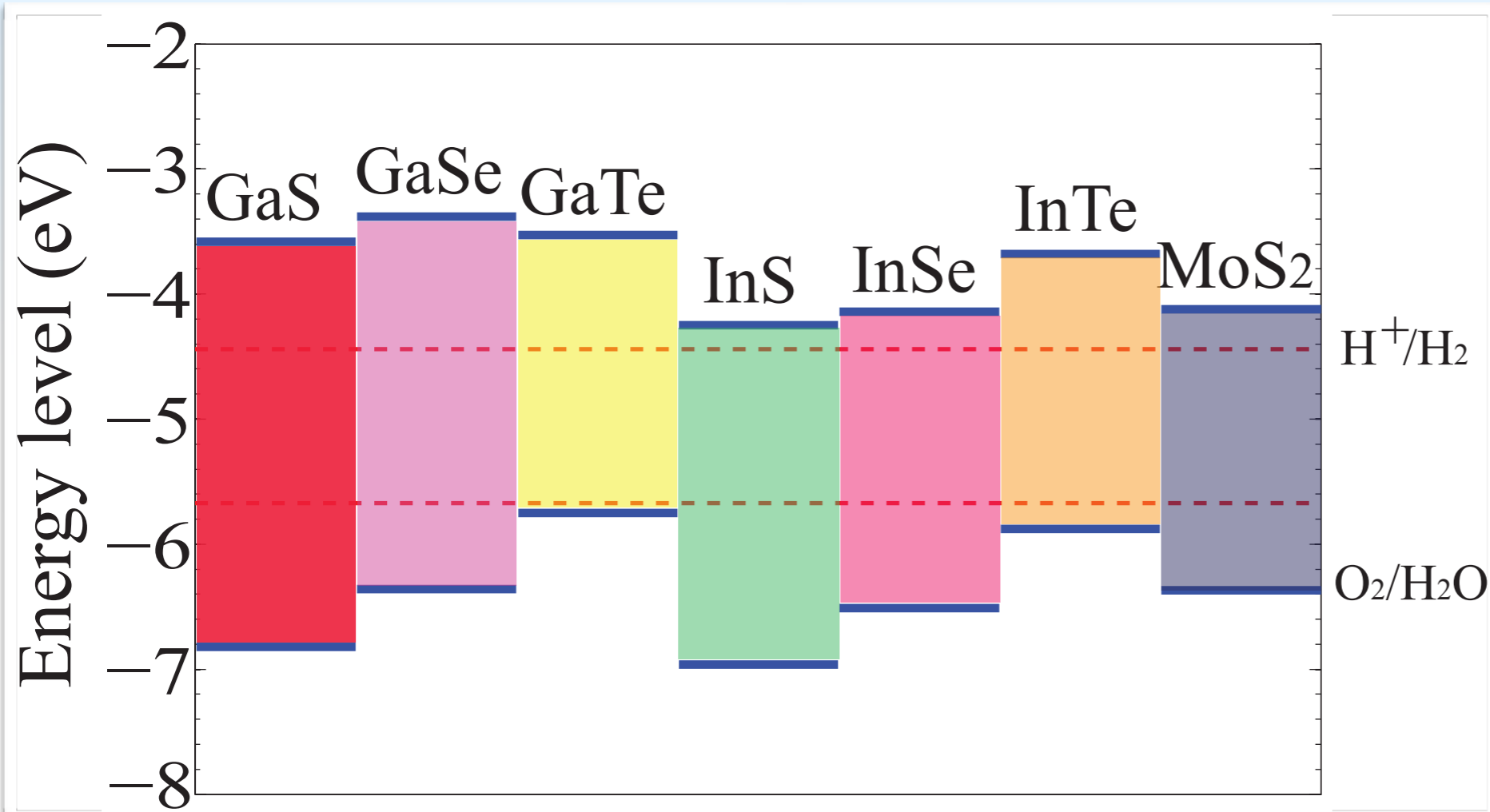
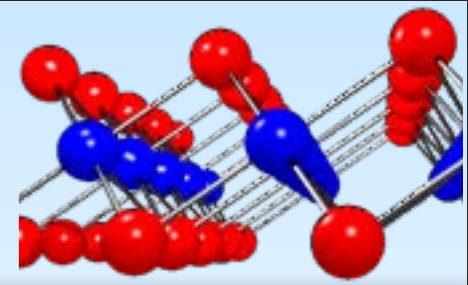
Another class of 2D materials



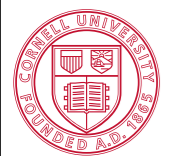
**Low formation energy indicates possible synthesis  
on suitable substrates**



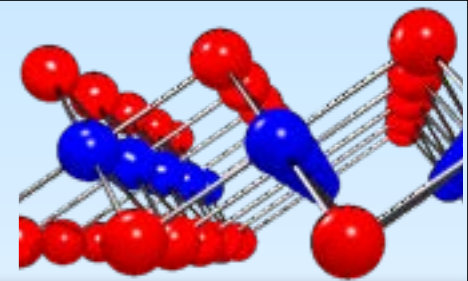
# Band Alignment with Water Potentials



**Monochalcogenides suitable for water splitting**  
**Band gap and alignment can be tuned by strain and pH**

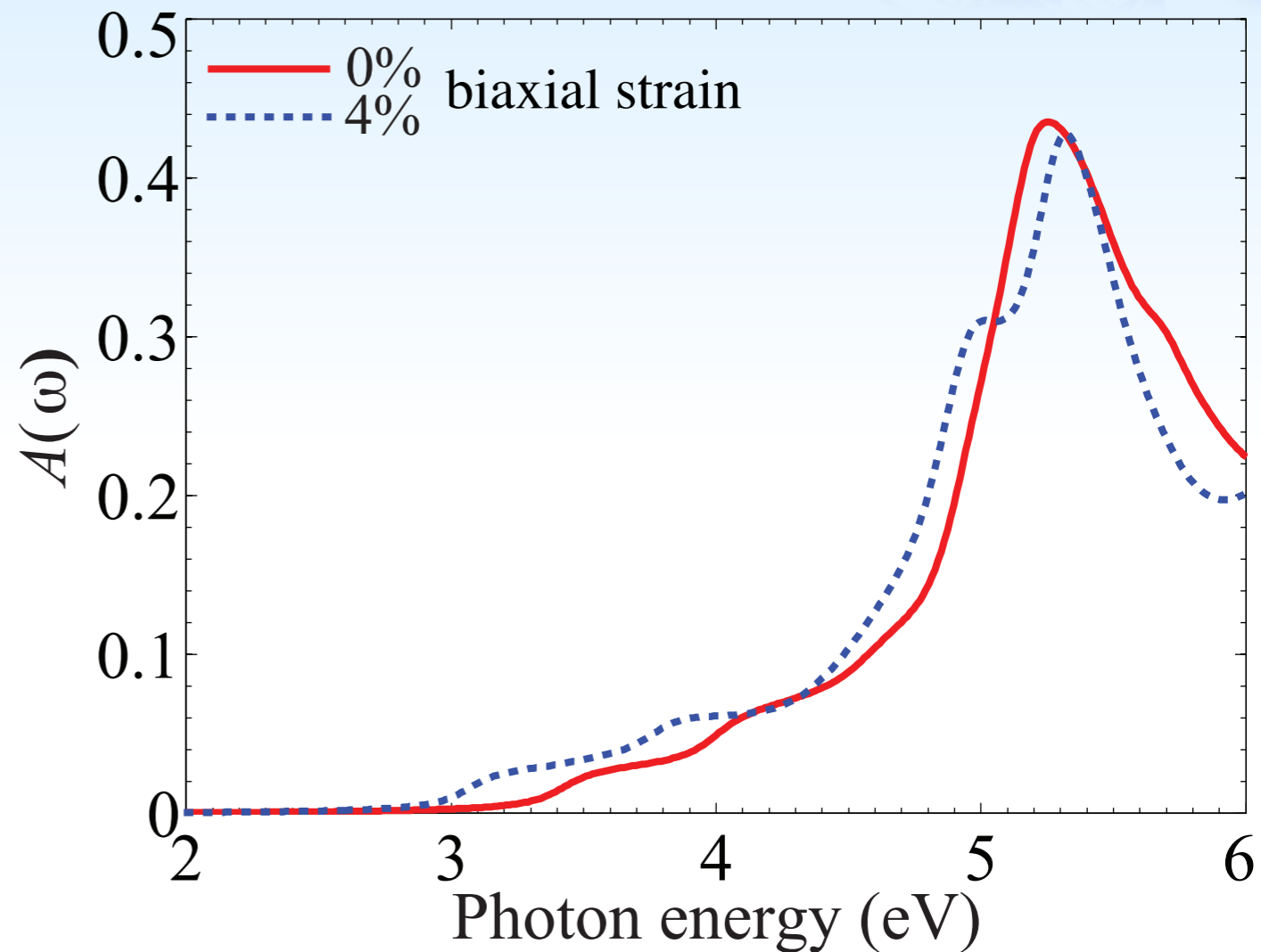


# Optical Absorption of Monochalcogenides

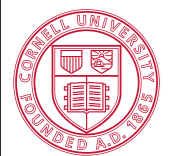


## Optical absorption of 2D GaSe

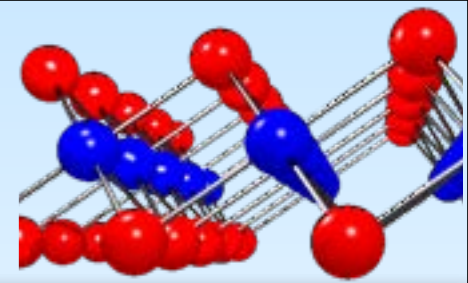
- Increases with energy over visible range up to 43%
- Strain further increases absorption
- Compare to graphene: 2.3% absorption



**Monochalcogenides have strong optical absorption**



# Stability in Aqueous Environment



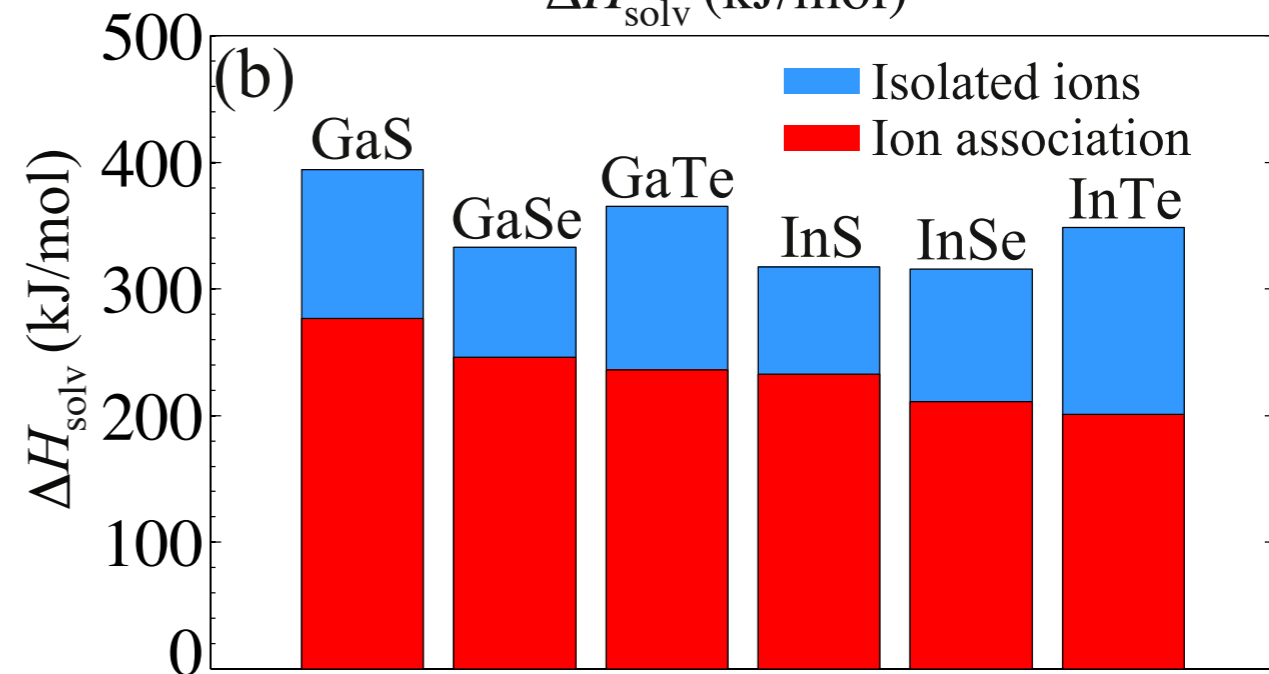
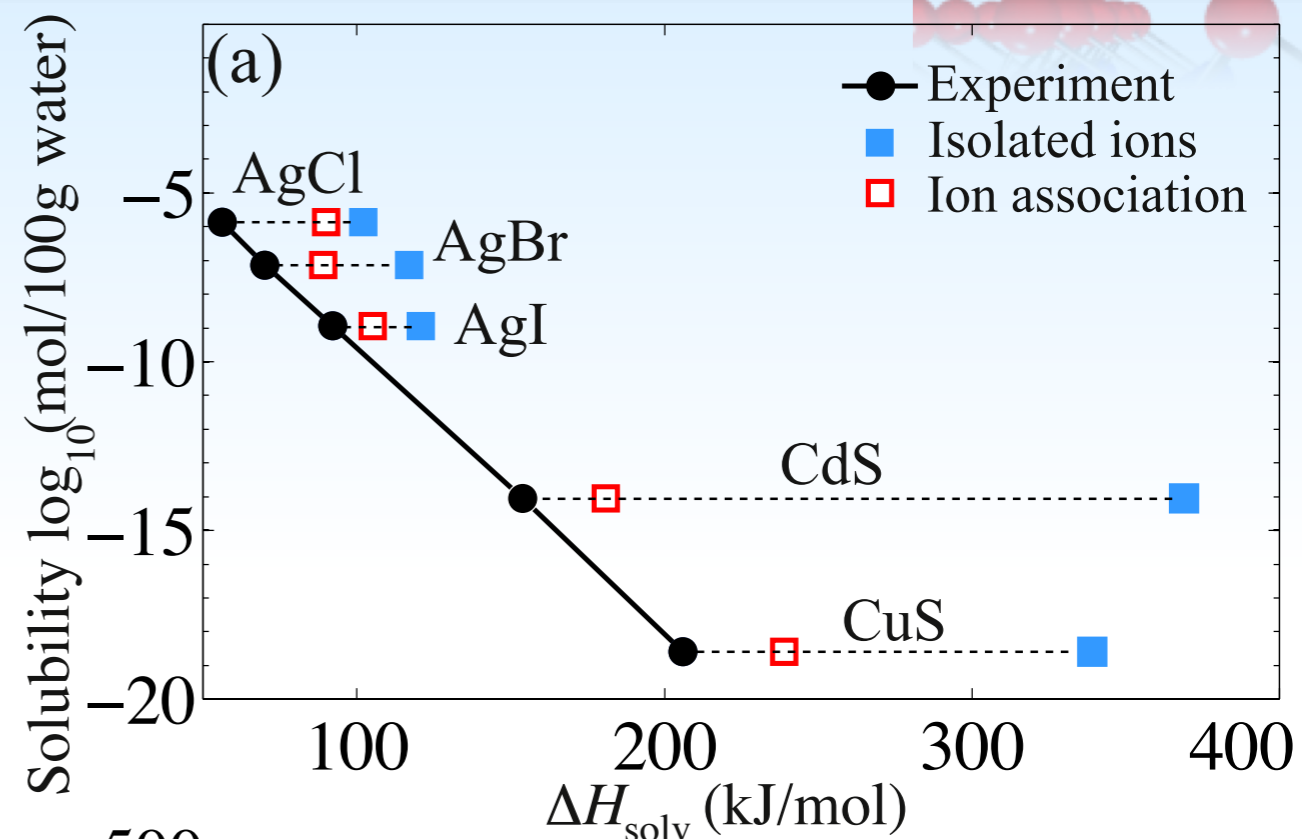
- High enthalpy of solvation indicates that group-III monochalcogenides are poorly soluble in water

## Next step:

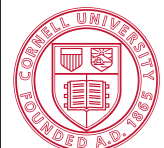
- Genetic algorithm searches for novel structures and unusual compositions

## Future work:

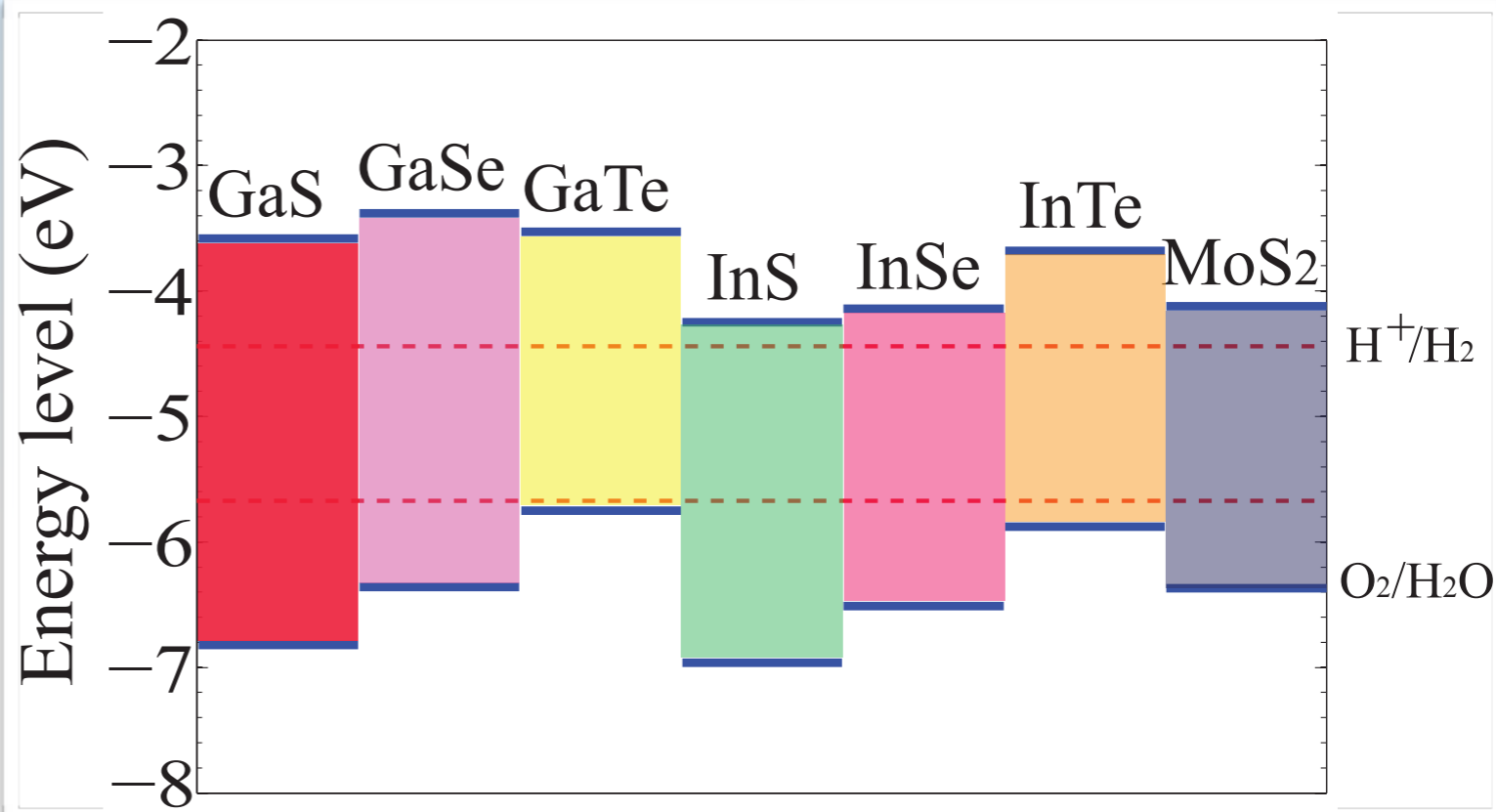
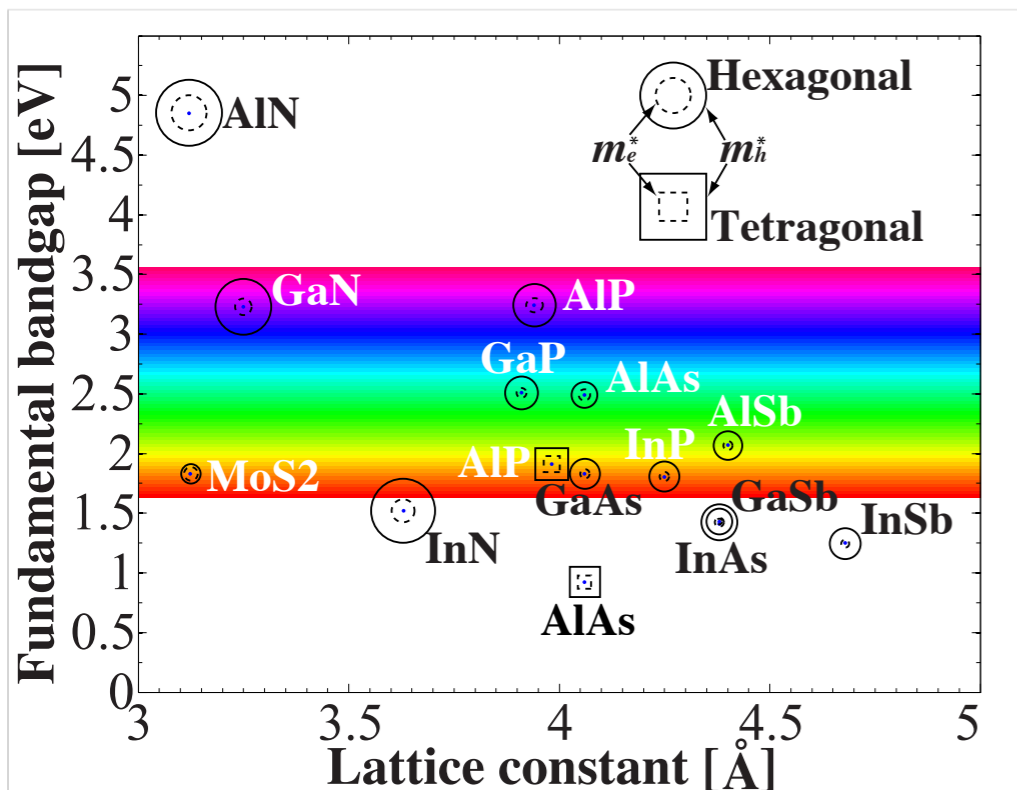
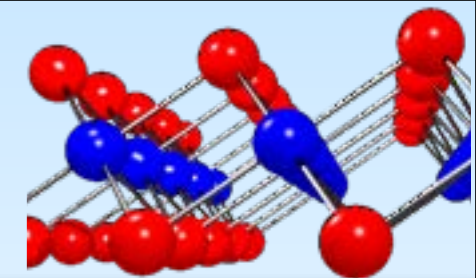
- Stability as a function of applied potential and pH, Pourbaix diagrams



Chemistry of Materials 25, 3232 (2013)



# Discovery of Single-layer materials



**Novel 2D materials with low formation energies show unique structures that can be stabilized on metal substrates, have useful electronic properties that can be tuned by strain, and can be stable in aqueous environment**

Appl. Phys. Lett. 101, 153109 (2012), Phys. Rev. B 87, 165415 (2013),  
 Chem. Mater. 25, 3232 (2013), Phys. Rev. B in print (2013), J. Phys. Chem. C in print (2013)

